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13. ABSTRACT (Maximum 200 words)

We have deposited molecules that behave as molecular switches into alkanethiol and amide-containing alkanethiol monolayers and have followed their behavior as a function of time, chemical substitution, environment, matrix order, and matrix thickness. We have shown that we can control this switching and that we can stabilize the conductance states through interactions with the surrounding matrix (see ppt slides). This is done via hydrogen-bonding interactions.

We have measured intermolecular interactions quantitatively by following the motion of adsorbed molecules.

We have developed methodologies to record thousands of single molecule measurements using scanning tunneling microscopy that have enabled all the above measurements.

We have designed monolayers that have weak intermolecular interactions and are thus labile with respect to displacement for use in patterning surfaces, and have demonstrated the utility of this approach.

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**ARMY RESEARCH OFFICE**

**FINAL REPORT**

**PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT**

for

GRANT or CONTRACT:
DAAD19-99-1-0269

Control of Structures and Properties in Ultrathin Films

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## I. Program Objectives

The objective of this program is to place molecules on surfaces, to change the properties of single molecules, and to measure these changes. Included are measurements of molecules whose conductance can be changed using an electric field as well as potentiometry of molecules between nanometer-scale electrodes.

## II. Selected Significant Results (also see included powerpoint file and notes)

This recently completed grant built up our foundation, knowledge, and abilities in controlling and measuring the molecules placed on surfaces. In this work, we advanced the field of nano-scale science in chemistry, chemical analyses, dynamics, electronics, physics, and materials. We studied and made fundamental discoveries in self-assembly,[1-21] chemical interactions,[22-28] molecular electronic properties,[1,2,6,15-18,29-33] and catalysis,[26,34-36] all on the atomic scale. We have developed means to control the placement of single molecules within films so as to tailor the local film properties.[10,18,19] We have developed new atomic-scale tools and methods[33,38] that we now apply to areas such as molecular motion,[22-26] molecular electronics,[1-3,6,15-18,29-33] and quantifying intermolecular interactions.[22-28] Selected significant advances in supported areas are detailed below.

### II.A. Single Molecule Electronics

We have demonstrated the ability to examine the electronic properties of molecules in terms of device properties.[6] This has led us to the design of molecules that interact with their surroundings so as to stabilize one or another electronic (conductance) state.[1,2]

Our first major paper on single molecule conductance switches, published early in this most recent funding period, established that single molecules could function as switches and elucidated the mechanism of switching.[6] The only mechanism that remains consistent with all the data is that the molecule-substrate bond conjugation changes, and this affects the conductacne of the molecule (see schematic in powerpoint file). This work was widely covered (*e.g.*, *New York Times*, *C&E News*, etc.).

We have since gone further in designing molecules to test other hypothesized mechanisms of function by including or excluding key functional groups and following these with measurements of the function (see attached powerpoint file).[3] These advances were enabled by our ability to measure many thousands of switching events for a given molecular design and set of conditions.[33] Our most recent work extends our dynamic range down to the millisecond time scale. We will now work to measure orders of magnitude faster.

The PI was chosen as Chair of the next international meeting in Molecular Electronics (January 2007).

### II.B. Manipulation of Atoms on and under the Substrate Surface

We have observed and manipulated H atoms beneath the surface of a Pd{111} crystal using low-temperature scanning tunneling microscopy. We demonstrated that the subsurface region of Pd can be populated with H atoms from the bulk by applying voltage pulses from a scanning tunneling microscope tip (see Fig. 1 and attached powerpoint files). We explained this phenomenon as being due to inelastic excitation whereby H atoms in the bulk are excited by tunneling electrons and are promoted to more stable sites in the subsurface region. Note that these subsurface H atoms are postulated to play critical roles in hydrogenation reactions, hydrogen storage, and metal embrittlement. They have not previously been observed nor placed directly.

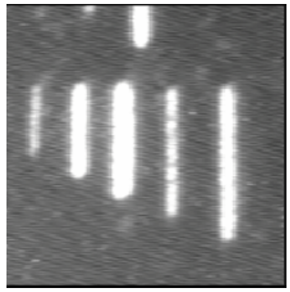

*Figure 1. Hydrogen can be selectively placed in subsurface sites on Pd{111} using inelastic scattering of absorbed H atoms. The dipole associated with the hydride and the significantly altered electronic structure are all measurable with STM. In this way, the reactivity and electronic structure of normal Pd and perturbed Pd can be measured simultaneously and side by side. Image: 1000 Å x 1000 Å, $V_{sample}$ = -25 mV, $I_{tunnel}$ = 50 pA, T = 4 K.*

**II.C. Chemical Interactions through Substrate Electronic Structural Perturbations**

We have discovered that isolated molecules on surfaces perturb their surroundings sufficiently to enhance reactions, catalysis, and binding.[22,23,25-28] We have shown how these perturbations enable growth of atomically precise structures and direct surface chemistry.

Our most recent work shows that the effects of these perturbations persist well above room temperature (300 °C) and direct the placement of adsorbates tens of Å apart. We did this by using a strongly perturbing adsorbate (Br adatoms on Cu{111}) that only diffuse at these elevated temperatures (see Fig. 2).

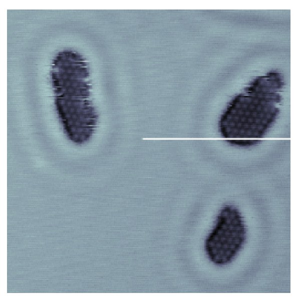

*Figure 2. Bromine islands remain after bromobenzene is dissociatively chemisorbed on Cu{111} and the phenyl has been converted to biphenyl and desorbed at 300 °C. At elevated temperatures, the Br adatoms are mobile and form islands. The island spacings are determined by the perturbed electronic structure due to neighboring islands. These large structures enable us to observe the electronic perturbations (the apparent "waves" between the islands in STM images) and determine the constructive and destructive interference due to the electronegative halogen atoms, which are simultaneously imaged with atomic resolution. The coherence length of the surface state electrons at the temperature at which the Br adatoms are mobile determines the lengths over which the island spacings are coupled to one another. Image: 176 Å x 176 Å, $V_{sample}$ = -0.20 V, $I_{tunnel}$ = 50 pA, T = 4 K.*

Another critical advance in this area and with broad implications has been our ability to automate data acquisition and analysis.[33] We have done this for benzene on Au{111} in order to determine the types of motion and the interaction strength between molecules and between molecules and the STM tip.[24,25] We can correlate the structural changes with site occupation and will show how these long-range interactions can result in the concerted motions of many molecules.

### II.D. New Tools and Methods

Our major instrumentation advance in this latest funding period, as mentioned above, has been advanced image processing techniques that extend the scientific capabilities of STM. A digital image tracking algorithm based on Fourier-transform cross-correlation has been developed to correct for instrumental drift in scanning tunneling microscope images.[38,33] This tracking algorithm was used to monitor conductance changes associated with different conformations in conjugated switching molecules and to trace the diffusion of individual molecules. It was then used to track and to separate correlated motions of many molecules. It has been picked up by other groups as a means to follow motion and to associate it with other observations.

## III. Training

Many undergraduate and graduate students, and post-docs have trained in our laboratory to work on these projects -- well beyond those supported by these ARO funds (e.g. through REU programs, ACS student fellowships, etc.). We have stretched and leveraged our ARO funds to the greatest extent possible to enable this.

## IV. Awards and Honors Resulting from this Work (28)

Takao Ishida
- New Energy Development Organization of Japan (NEDO) Fellow, 2003.

Jennifer J. Jackiw
- Named Assistant Professor of Forensics, John Jay School of Law.

S. Alex Kandel
- Named Assistant Professor of Chemistry, Notre Dame University

Kevin F. Kelly
- Named Assistant Professor of Electrical and Computer Engineering, Rice University

Penelope Lewis
- Braucher Scholarship, 2001.

Brent A. Mantooth
- Geiger Fellowship, 2001.
- Weyenberg Award, 2002.
- American Chemical Society, Division of Analytical Chemistry Graduate Fellowship, 2003-2004.
- Miller Fellowship, 2004.
- Named Senior Scientist with tenure, Geo-Centers Research Laboratories.

Greg McCarty
- Named Assistant Professor of Engineering Science and Mechanics, Penn State University.

Jason D. Monnell
- Named Research Assistant Professor of Environmental Engineering, University of Pittsburgh.

Sanjini Nanayakkara
- American Vacuum Society, Dorothy and Earl Hoffmann Award Finalist & Travel Grant, 2003.
- American Vacuum Society, Dorothy and Earl Hoffmann Award Finalist & Travel Grant, 2004.
- Pittsburgh-Cleveland Catalysis Society, 42$^{nd}$ Annual Symposium, Best Student Talk, 2004.

Thomas P. Pearl
- Named Assistant Professor of Physics, North Carolina State University, 2003.

E. Charles H. Sykes
- Materials Research Institute Post-doctoral Research Award, 2004.
- Named Assistant Professor of Chemistry, Tufts University, 2005.

Alexander Wissner-Gross*
- Intel Research Award for Undergraduate Students, 2001.

Intel Research Contest for Undergraduate Students, 1st Place, 2002.
Marshall Scholar, 2003.
USA Today All-USA 1st College Academic Team, 2003.
Hertz Foundation Fellow, 2003.

Paul S. Weiss
Promoted to Professor, Department of Chemistry, Pennsylvania State University, 2001.
Named Professor, Department of Physics, Pennsylvania State University, 2002.
American Physical Society, Elected Fellow, 2002.
Penn State, Eberly College of Science Graduation, Faculty Marshal (2002).
Penn State, Schreyer Honors College Excellence in Honors Teaching Award (2004).

**Undergraduate participating in NSF-sponsored research.*

## V. Service

### V.A. Interactions with the US Army, Other Services, and Related Federal and Private Activities

Office of the Secretary of Defense Technical Area Review and Assessment for Chemical and Biological Defense Research Programs, 1999, 2000.
Workshop on Advanced Technologies and Future Joint Warfighting, Nanotechnology and Chemical Systems Panel Co-chair, Alexandria, VA, 1999.
Defense Science Board, 21st Century Defense Technology Strategies Summer Study, Intelligence Needs and Adversaries Task Force, 1999.
U. S. Army Soldier, Biological, and Chemical Command, Biotechnology Advisory Panel, 2000.
Defense Science Board, Homeland Defense Summer Study, Intelligence Needs for Civil Support Task Force, 2000-2001.
U. S. Army Chemical and Biological Agent Resistance Testing Technical Advisory Panel, 2001-.
Naval Studies Board, Office of Naval Research Marine Corps Science and Technology Program, 2003.
Institute for Defense Analysis, Alexandria, VA, Consultant, 1996-.
Science and Technology Policy Institute, Alexandria, VA, Consultant, 2003-.

### V.B. Other Related Service

STM '99, Tenth International Conference on Scanning Tunneling Microscopy, Seoul, Korea, July 18-23, 1999, program committee.
International Union of Materials Research Societies - International Conference in Asia 2000, July 24-26, 2000, Hong Kong, symposium co-organizer for: "Scanning Probe Microscopy for Materials Characterization."
International Conference on Molecular Electronics, Kona, HI, December 10-14, 2000, organizing committee.
Pacifichem 2000, Honolulu, HI, December 14-19, 2000, symposium co-organizer for: "Ordered Molecular Films."
2001 Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Detroit, MI, October 10, 2001, symposium organizer for: "Scanning Probe Microscopy."
The 1st U.S.-Korea Workshop on Nanofabrication Science and Technology, Co-chair, Seoul, Korea, June 3-5, 2002.
39th Annual Technical Meeting, Society of Engineering Science, Nanofabrication and

Nanotechnology and Nanofabrication Symposium Co-organizer, University Park, PA, October 13 - 16, 2002.

Materials Research Society, San Francisco, CA, symposium co-organizer: Molecular Electronics, March 2003.

Crossover 2004, University Park, PA, organizing committee, October 20-21, 2004.

Foundations of Nanoscience 2005, Snowbird, UT, symposium organizer and track co-chair: Surface functionalization, April 2005.

Fifty Years of Imaging the Atom, University Park, PA, co-organizer, June 17-18, 2005.

SPIE Conference on Imaging and Metrology at the Nanoscale, San Diego, CA, conference chair, July 31-August 4, 2005.

Crossover 2005, University Park, PA, organizing committee, October, 2005.

Foundations of Nanoscience 2006, Snowbird, UT, conference technical co-chair, April, 2006.

8$^{th}$ International Meeting on Molecular Engineering, Chair, January, 2007.

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2. "Molecular Engineering of the Polarity and Interactions of Molecular Electronic Switches," P. A. Lewis, C. E. Inman, F. Maya, J. M. Tour, J. E. Hutchison, and P. S. Weiss, to be submitted.
3. *Conductance Switching for a Variety of Conjugated Molecules*, A. M. Moore, A. A. Dameron, B. A. Mantooth, J. W. Ciszek, F. Maya, J. M. Tour, and P. S. Weiss, submitted for publication.
4. "Phase Separation of Mixed-Composition Self-Assembled Monolayers into Nanometer Scale Molecular Domains," S. J. Stranick, A. N. Parikh, Y.-T. Tao, D. L. Allara, and P. S. Weiss, *Journal of Physical Chemistry* **98**, 7636 (1994).
5. "Micro-Displacement Printing," A. A. Dameron, J. R. Hampton, R. K. Smith, T. J. Mullen, and P. S. Weiss, submitted to *Nano Letters*.
6. "Conductance Switching in Single Molecules through Conformational Changes," Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price, A. M. Rawlett, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **292**, 2303 (2001).
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8. "The Role of Buried Hydrogen Bonds in Self-Assembled Mixed Composition Thiols on Au{111}," P. A. Lewis, R. K. Smith, K. F. Kelly, L. A. Bumm, S. M. Reed, R. S. Clegg, J. D. Gunderson, J. E. Hutchison, and P. S. Weiss, *Journal of Physical Chemistry B* **105**, 10630 (2001).
9. "Structures and the Displacement of 1-Adamantanethiol Self-Assembled Monolayers on Au{111}," A. A. Dameron, L. F. Charles and P. S. Weiss, *Journal of the American Chemical Society* (2005), in press (now available via *JACS* ASAP).
10. "Are Single Molecular Wires Conducting?" L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **271**, 1705 (1996).
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32. "Nanometer-Scale Electronics and Storage," K. F. Kelly, Z. J. Donhauser, B. A. Mantooth, and P. S. Weiss, in *Scanning Probe Microscopy: Characterization, Nanofabrication, and Device Application of Functional Materials*, edited by P. M. Vilarinho, Y. Rosenwaks, and A. Kingon, *NATO Science Series II: Mathematics, Physics and Chemistry* **186**, 152 (Kluwer Academic, 2005).
33. "Cross-Correlation Image Tracking for Adsorbate Analysis and Drift Correction," B. A. Mantooth, Z. J. Donhauser, K. F. Kelly, and P. S. Weiss, *Review of Scientific Instruments* **73**, 313 (2002).
34. "Mobile Promoters on Anisotropic Catalysts: Ni on $MoS_2$," J. G. Kushmerick and P. S. Weiss, *Journal of Physical Chemistry B* **102**, 10094 (1998).
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Patrick Han, Graduate Student
Jennifer J. Jackiw, Graduate Student
Penelope A. Lewis, Graduate Student
Brent A. Mantooth, Graduate Student
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Anat Hatzor, Post-doctoral Fellow
S. Alex Kandel, Post-doctoral Fellow
Kevin F. Kelly, Post-doctoral Fellow
Thomas P. Pearl, Post-doctoral Fellow
E. Charles H. Sykes, Post-doctoral Fellow

## VIII. Publications Resulting from this Project (31)


1. *Molecular Rulers for Scaling Down Nanostructures*, A. Hatzor and P. S. Weiss, *Science* **291**, 1019–1020 (2001).
2. *Molecular Scale Electronics*, A. M. Rawlett, E. T. Mickelson, W. A. Reinerth, L. Jones II, M. Kozaki, T. P. Burgin, and J. M. Tour, J. Chen, C.–W. Zhou, C. J. Muller, M. R. Deshpande, M. A. Reed, L. A. Bumm, M. T. Cygan, T. D. Dunbar, P. S. Weiss, and D. L. Allara, *Proceedings of the Materials Research Society* **582**, H.9.2.1–H.9.2.8 (2001).
3. *Conductance Switching in Single Molecules through Conformational Changes*, Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price, Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **292**, 2303–2307 (2001).
4. *Control and Placement of Molecules via Self-Assembly*, P. A. Lewis, Z. J. Donhauser, B. A. Mantooth, R. K. Smith, L. A. Bumm, K. F. Kelly, and P. S. Weiss, *Nanotechnology* **12**, 231–237 (2001).
5. *Molecules Join the Assembly Line*, P. S. Weiss, *Nature* **413**, 585–586 (2001).
6. *The Role of Buried Hydrogen Bonds in Self-Assembled Mixed Composition Thiols on Au{111}*, P. A. Lewis, R. K. Smith, K. F. Kelly, L. A. Bumm, S. M. Reed, R. S. Clegg, J. D. Gunderson, J. E. Hutchison, and P. S. Weiss, *Journal of Physical Chemistry B* **105**, 10630–10636 (2001).
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8. *Matrix-Mediated Control of Stochastic Single Molecule Conductance Switching*, Z. J. Donhauser, B. A. Mantooth, T. P. Pearl, K. F. Kelly, S. U. Nanayakkara, and P. S. Weiss, *Japanese Journal of Applied Physics* **41**, 4871–4877 (2002).
9. *Exploiting Intermolecular Interactions and Self-Assembly for Ultrahigh Resolution Nanolithography*, M. E. Anderson, R. K. Smith, Z. J. Donhauser, A. Hatzor, P. A. Lewis, L. P. Tan, H. Tanaka, M. W. Horn, and P. S. Weiss, *Journal of Vacuum Science and Technology B* **20**, 2739–2744 (2002).
10. *Controlling and Measuring Molecular-Scale Properties for Molecular Nanoelectronics*, R. K. Smith and P. S. Weiss, in *Molecular Nanoelectronics*, T. Lee and M. Reed, eds., 153–177 (American Scientific Publishers, Stevenson Ranch, CA, 2003).
11. *Control of Alkanethiolate Monolayer Structure Using Vapor-Phase Annealing*, Z. J. Donhauser and P. S. Weiss, *Journal of the American Chemical Society* **125**, 11462–11463 (2003).
12. *Fabrication, Assembly and Characterization of Molecular Electronic Components*, B. A. Mantooth and P. S. Weiss, *Proceedings of the IEEE* **91**, 1785–1802 (2003).
13. *Advances in Nanolithography Using Molecular Rulers*, M. E. Anderson, L. P. Tan, H. Tanaka, M. Mihok, H. Lee, M. W. Horn, and P. S. Weiss, *Journal of Vacuum Science and Technology B* **21**, 3116–3119 (2003).
14. *Substrate-Mediated Interactions and Intermolecular Forces between Molecules Adsorbed on Surfaces*, E. C. H. Sykes, P. Han, S. A. Kandel, K. F. Kelly, G. S. McCarty, and P. S. Weiss, *Accounts of Chemical Research* **36**, 945–953 (2003).
15. *Patterning Self-Assembled Monolayers*, R. K. Smith, P. A. Lewis and P. S. Weiss, *Progress in Surface Science* **75**, 1–68 (2004).
16. *Position-Selected Molecular Ruler*, H. Tanaka, M. E. Anderson, M. W. Horn, and P. S. Weiss, *Japanese Journal of Applied Physics* **43**, L950–L953 (2004).
17. *Benzene on Au{111} at 4 K: Monolayer Growth and Tip-Induced Molecular Cascades*, P. Han, B. A. Mantooth, E. C. H. Sykes, Z. J. Donhauser, and P. S. Weiss, *Journal of the American Chemical Society* **126**, 10787–10793 (2004).
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19. *The Effects of Hindered Internal Rotation on Packing and Conductance of Self-Assembled Monolayers*, A. A. Dameron, J. W. Ciszek, J. M. Tour, P. S. Weiss, *Journal of Physical Chemistry B* **108**, 16761-16767 (2004).
20. *Expanding the Capabilities of the Scanning Tunneling Microscope*, K. F. Kelly, Z. J. Donhauser, B. A. Mantooth, and P. S. Weiss, in *Scanning Probe Microscopy: Characterization, Nanofabrication, and Device Application of Functional Materials*, edited by P. M. Vilarinho, Y. Rosenwaks, and A. Kingon, *NATO Science Series II: Mathematics, Physics and Chemistry* **186**, 152-171 (Kluwer Academic, 2005).
21. *Nanometer-Scale Electronics and Storage*, K. F. Kelly, Z. J. Donhauser, P. A. Lewis, R. K. Smith, and P. S. Weiss, in *Scanning Probe Microscopy: Characterization, Nanofabrication, and Device Application of Functional Materials*, edited by P. M. Vilarinho, Y. Rosenwaks, and A. Kingon, *NATO Science Series II: Mathematics, Physics and Chemistry* **186**, 333-354 (Kluwer Academic, 2005).
22. *Substrate-Mediated Intermolecular Interactions: A Quantitative Single Molecule Analysis*, E. C. H. Sykes, B. A. Mantooth, P. Han, Z. J. Donhauser, and P. S. Weiss, *Journal of the American Chemical Society* **127**, 7255-7260 (2005).
23. *Structures and the Displacement of 1-Adamantanethiol Self-Assembled Monolayers on Au{111}*, A. A. Dameron, L. F. Charles and P. S. Weiss, *Journal of the American Chemical Society* **127** (2005), in press, already available on *JACS* ASAP.
24. *Adsorption of CO on Ag{111} Mediated by the Interaction with Surface-State Electrons*, M. Kulawik, M. Heyde, H.-P. Rust, H.-J. Freund, B. A. Mantooth, and P. S. Weiss, *Surface Science Letters*, in press.
25. *Direct Observation and Manipulation of Subsurface Hydrogen in Pd{111}*, E. C. H. Sykes, L. C. Fernández-Torres, S. U. Nanayakkara, B. A. Mantooth, R. M. Nevin, and P. S. Weiss, submitted.
26. *Photolithographic Structures with Precise Controllable Nanometer-Scale Spacings Created by Molecular Rulers*, M. E. Anderson, L. P. Tan, M. Mihok, H. Tanaka, M. W. Horn, G. S. McCarty, and P. S. Weiss, submitted to *Nano Letters*.
27. *Micro-Displacement Printing*, A. A. Dameron, J. R. Hampton, R. K. Smith, T. J. Mullen, and P. S. Weiss, submitted to *Nano Letters*.
28. *Conductance Switching for a Variety of Conjugated Molecules*, A. M. Moore, A. A. Dameron, B. A. Mantooth, J. W. Ciszek, F. Maya, J. M. Tour, and P. S. Weiss, submitted for publication.
29. *Exploiting Intermolecular Interactions for Nanoscale Control*, P. S. Weiss, P. T. Hammond, and F. Moresca, invited manuscript in preparation for *Proceedings of the National Academy of Science*.
30. *Single Molecule Measurements*, B. A. Mantooth and P. S. Weiss, invited feature article in preparation for *Journal of Physical Chemistry B*.
31. *Substrate-Mediated Interactions and Intermolecular Forces between Molecules Adsorbed on Surfaces*, S. U. Nanayakkara and P. S. Weiss, invited manuscript in preparation for *Surface Science Reports*.

## IX. Patents Resulting from this Project

None.

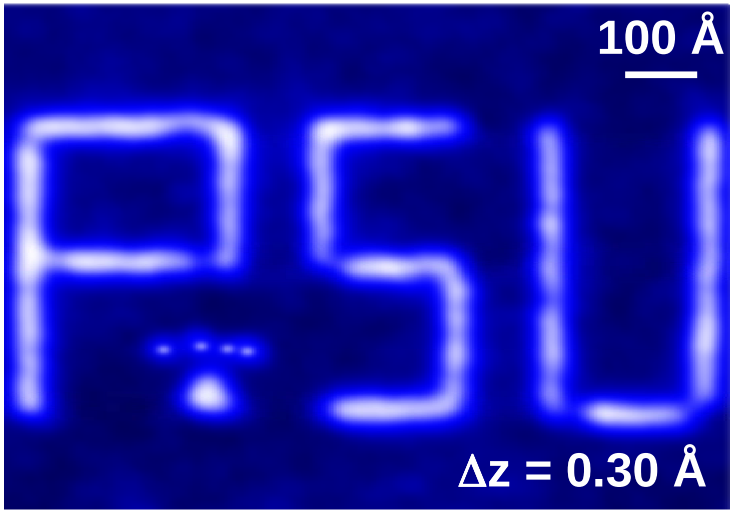
# Manipulation of Hydrogen on and under Pd{111}

**Paul S. Weiss**
Departments of Chemistry & Physics
The Pennsylvania State University
http://www.nano.psu.edu/

**H on Pd can both *<u>adsorb</u>* and *<u>absorb</u>* hydrogen – with different chemistries and electronic properties.**

**Critical to hydrogen storage and separation, catalysis, and embrittlement.**

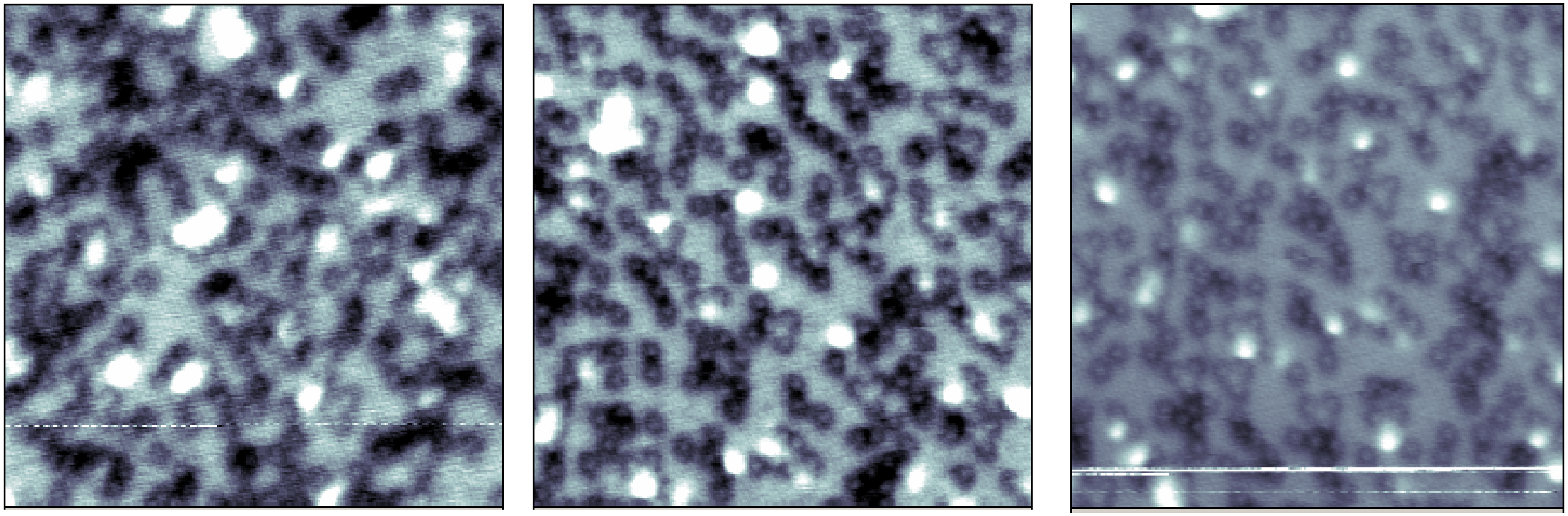
**Use STM (via inelastic tunneling) to move atoms on and underneath the surface.**






Sykes, Fernandez-Torres, Nanayakkara, Mantooth, Nevin & Weiss

# Adsorbed H on Pd {111}
# Bias Dependent Mobility



175 Å x 175 Å, 0.07 V, 50 pA | 175 Å x 175 Å, 0.1 V, 50 pA | 175 Å x 175 Å, 0.15 V, 50 pA

**Increasing bias**

**Onset for hydrogen mobility = ±0.1 eV**

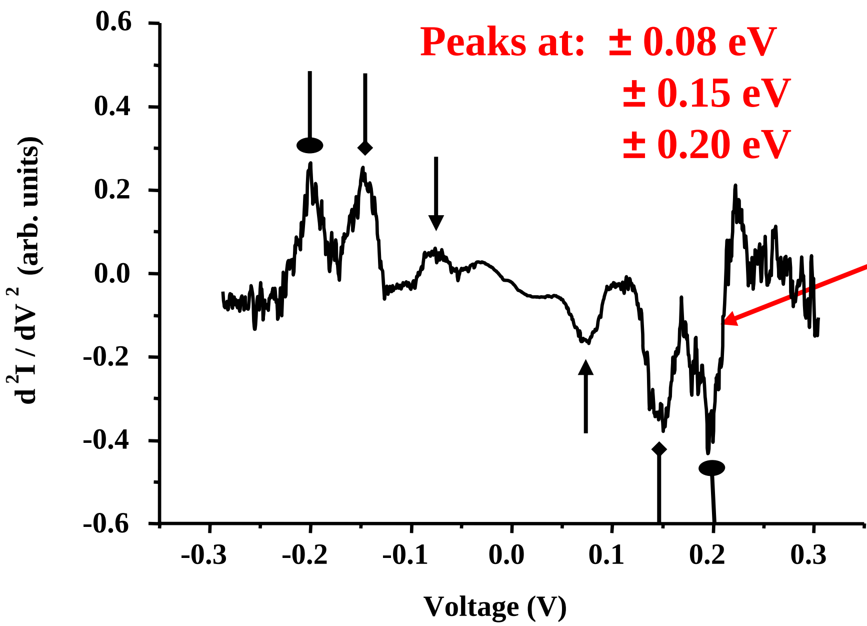
***(linked movies of mobile atoms at high bias)***

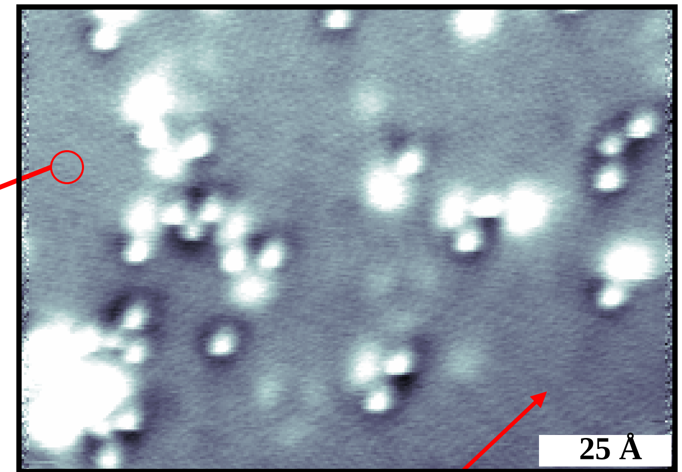
PS Weiss

**Sykes, Fernandez-Torres, Nanayakkara, Mantooth, Nevin & Weiss**

# Vibrational Spectroscopy of H Atoms on Pd{111} Using Scanning Tunneling Spectroscopy

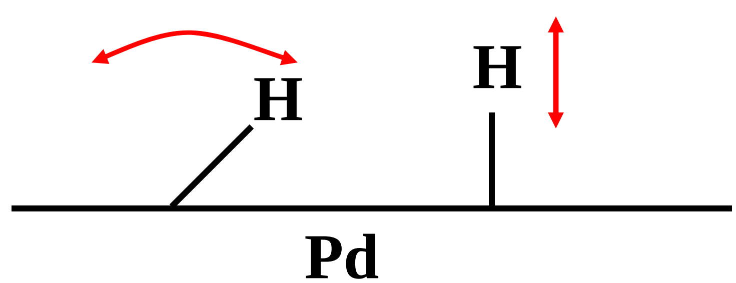
## IETS Spectra over H-Pd bond




**V = -15 mV, I = 200 pA, 100 Å × 80 Å**

**(1x1) Hydrogen (dark areas)**



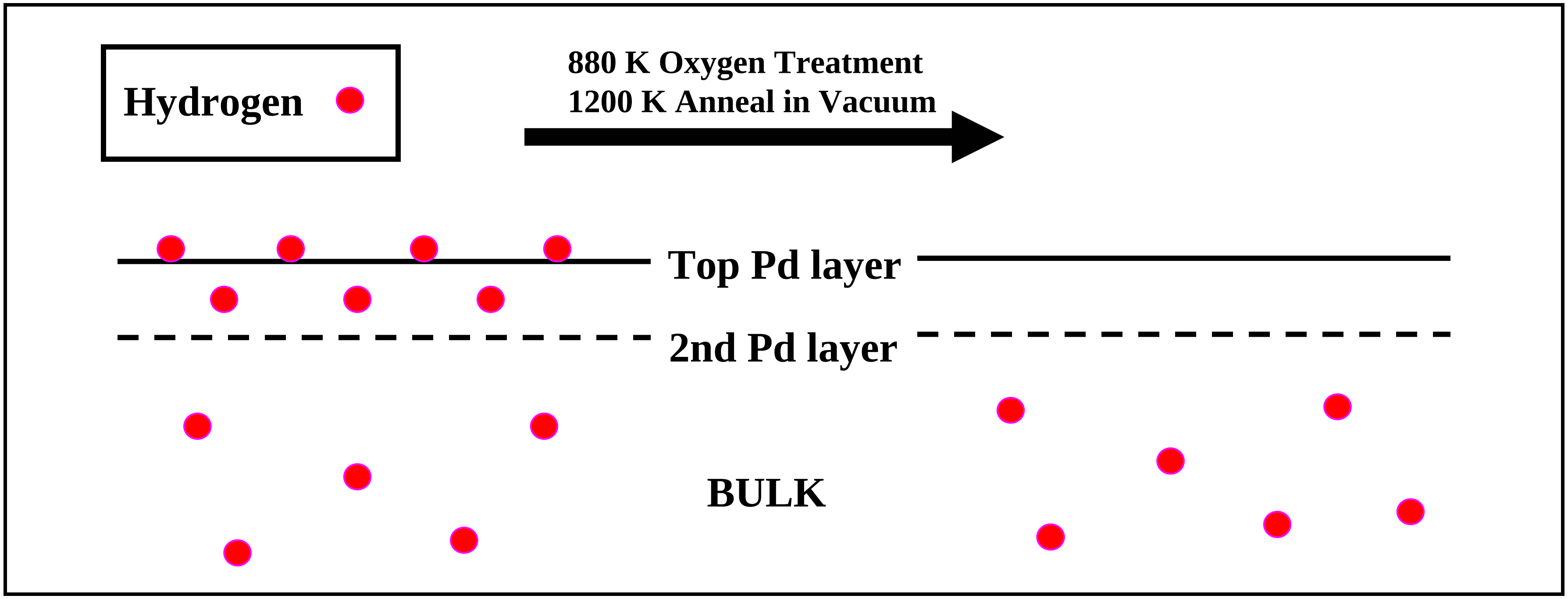

**HREELS of H-Pd{111}:**

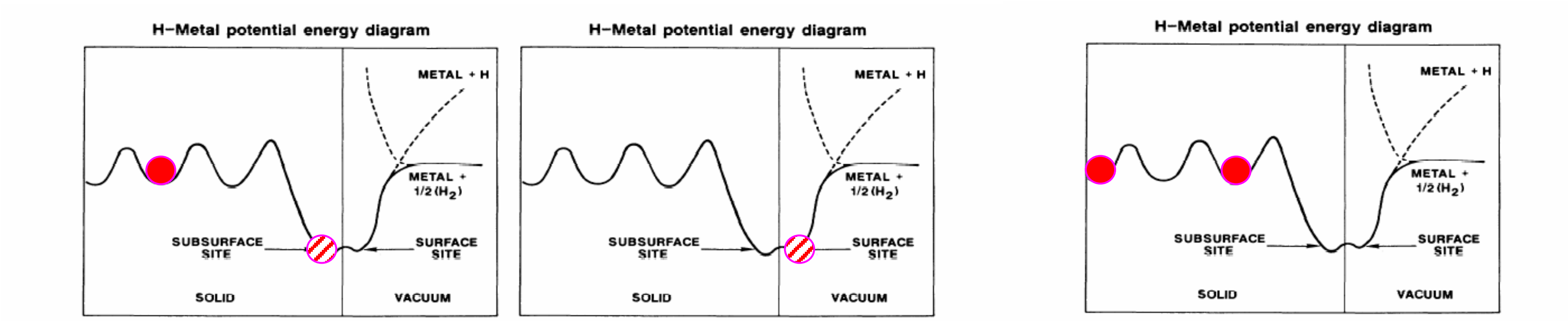
**0.096 eV – parallel mode**
**0.124 eV – perpendicular mode**

**(Stenzel, *J. Electron. Spectr. Related Phenom.* 1986)**

PS Weiss

# Subsurface H *in* Pd{111}



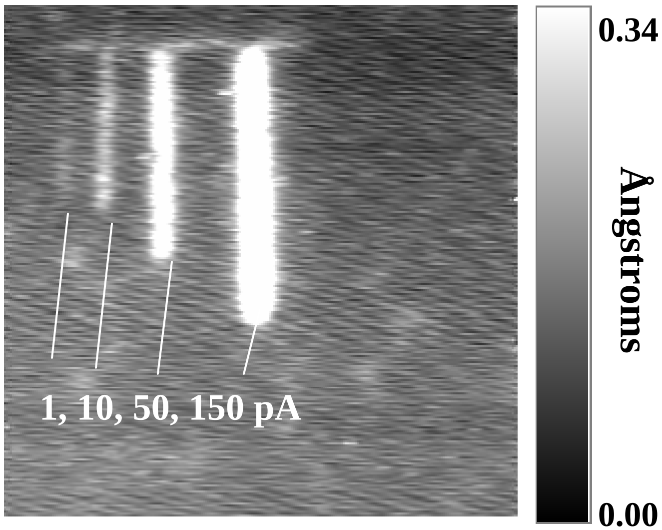




**STABLE** **METASTABLE**

PS Weiss

# Placing H in Selected Locations *in* Pd{111}

**CURRENT DEPENDENCE**

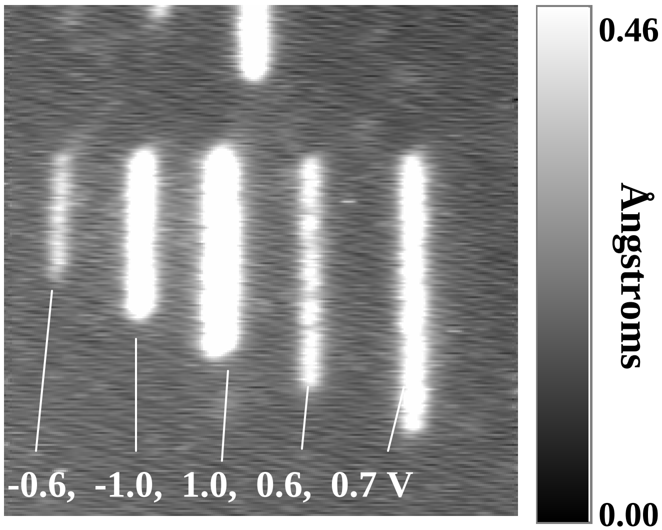



**V = -25 mV, I = 50 pA, 1000 Å × 1000 Å**

**Increasing Current**

**@ -0.7 V**

**VOLTAGE DEPENDENCE**




**V = -25 mV, I = 50 pA, 1000 Å × 1000 Å**

**Bias Dependence (Onset ~ 0.5 V )**

**@ 50 pA**

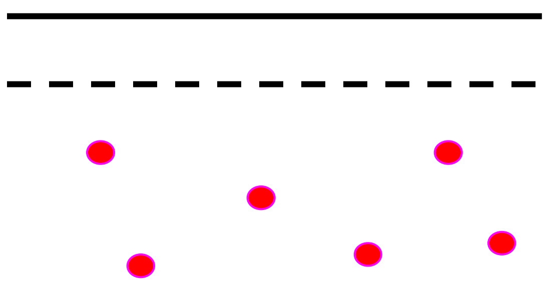
**LINE Width = f(tip shape, available H in bulk)**

**Features are much smaller that 1500 Å mean free path of electrons in Pd, because H atoms are scatterers**

PS Weiss

**Sykes, Fernandez-Torres, Nanayakkara, Mantooth, Nevin & Weiss**

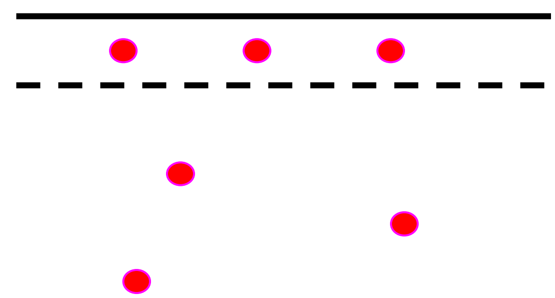
# Placing H in Selected Locations *in* Pd{111}

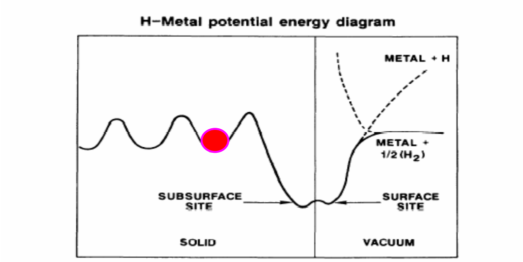


Top Pd layer

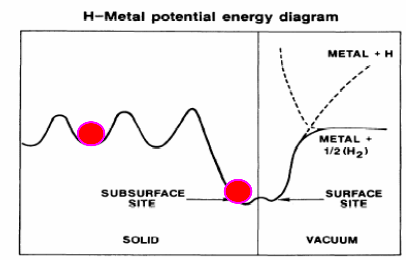
2nd Pd layer

BULK



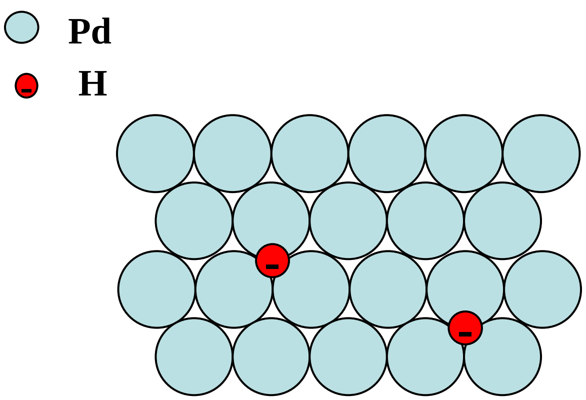



Tip-Induced H Segregation



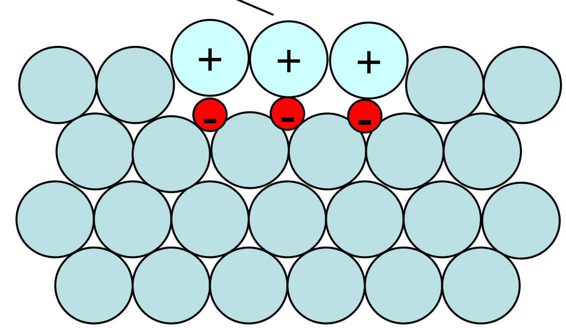

**METASTABLE**

**STABLE**




[111] Direction

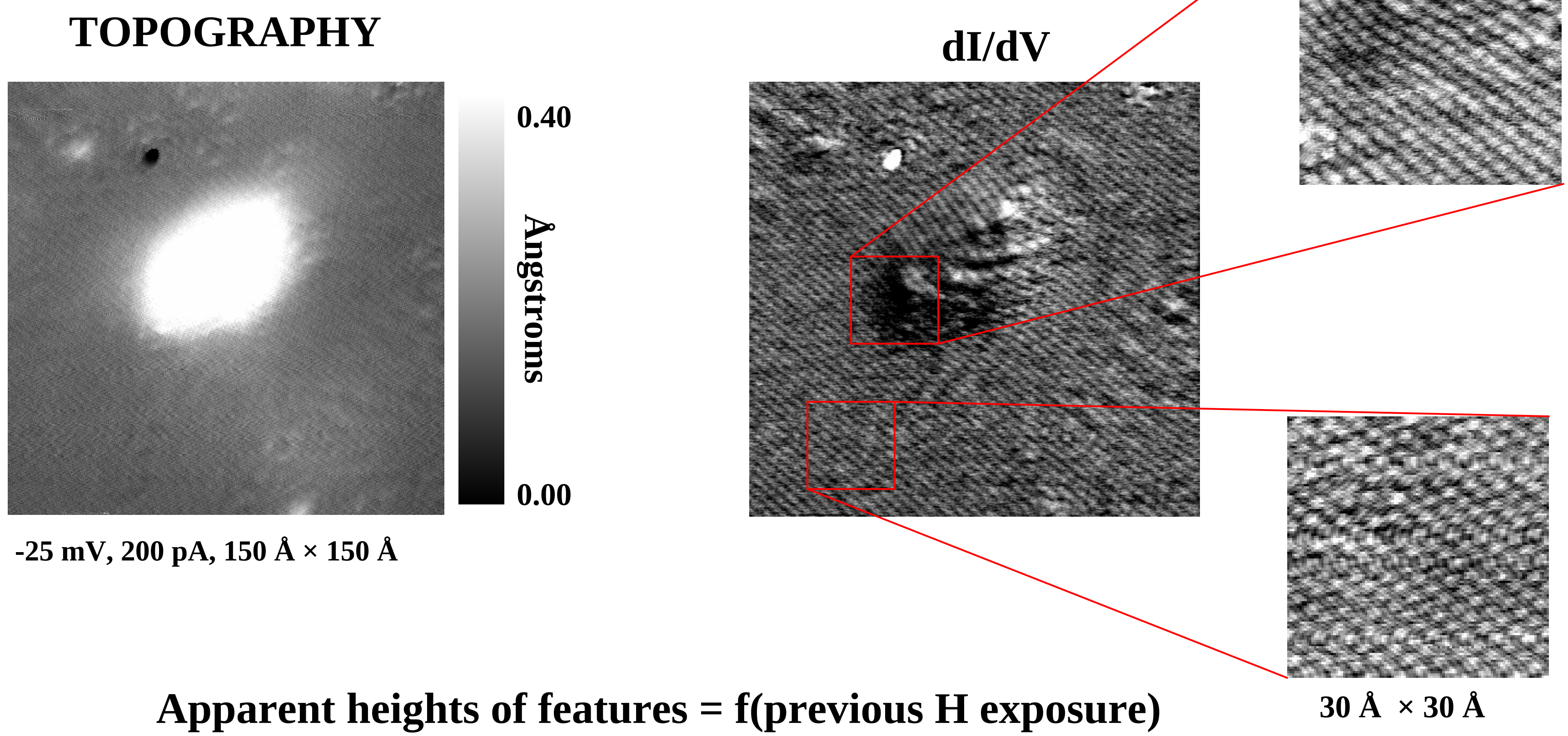
TOPOGRAPHICALLY HIGH
ELECTRONICALLY LOW



PS Weiss

# Measuring H *in* Pd{111}

**Distortion of both lattice and electronic structure are observed after selective placement of subsurface H**




**Apparent heights of features = f(previous H exposure)**

**Therefore different amounts of H are present in the bulk**



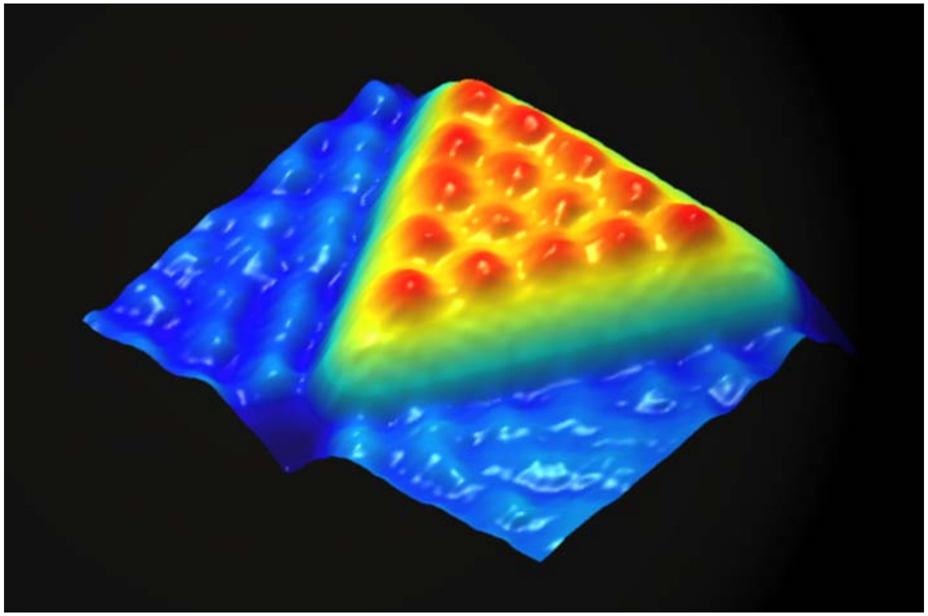
**Sykes, Fernandez-Torres, Nanayakkara, Mantooth, Nevin & Weiss**

# Substrate-Mediated Interactions

**Paul S. Weiss**
**Departments of Chemistry & Physics**
**The Pennsylvania State University**
**http://www.nano.psu.edu/**

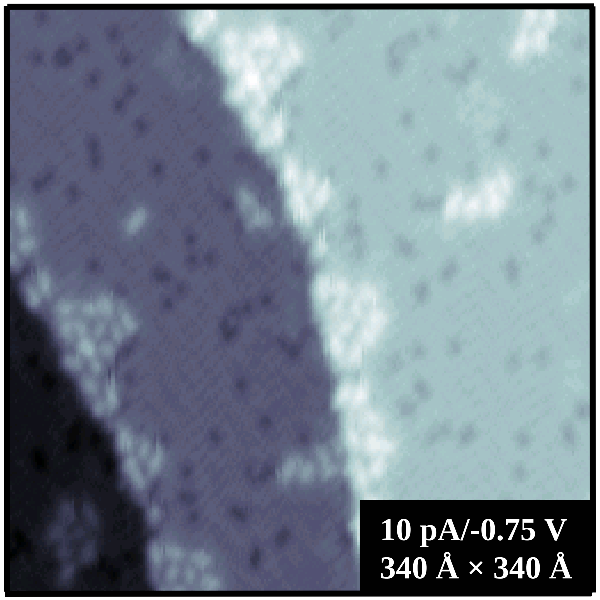
**Use spectroscopic capability of the scanning tunneling microscope to map spatial distribution of electronic structure.**

**Allow mobile probe (or reactant) molecules to sample these potentials.**

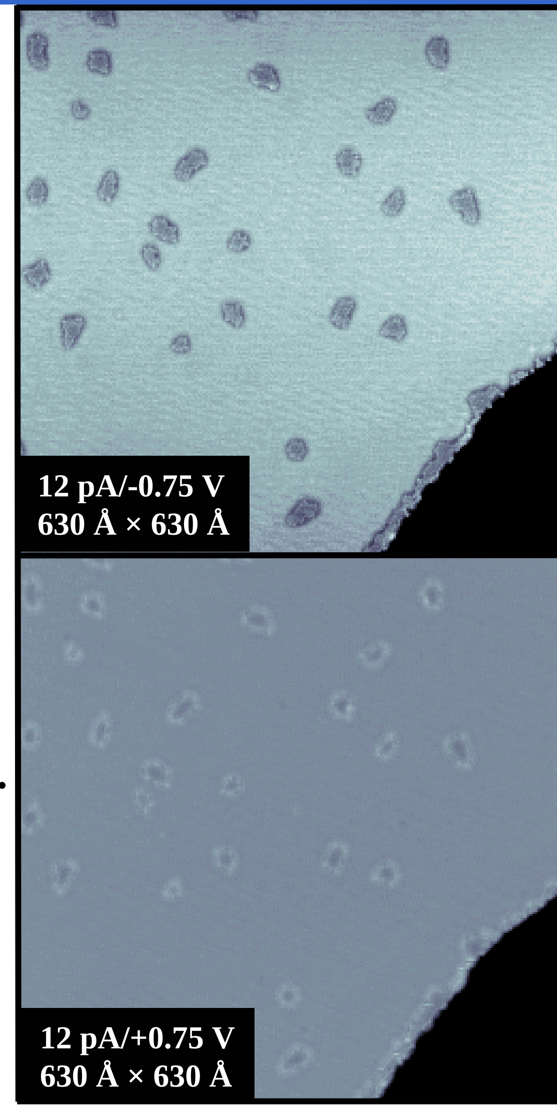


**Au{111}**
**130 Å x 130 Å**
**$V_{Sample} = -0.5$ V**
**I = 10 pA**
**T = 4 K**

# Substrate-Mediated Interactions above Room Temperature: Br on Cu{111}




593 K / 300 °C




Dose with bromobenzene to form phenyl and Br.
Desorb biphenyl at 390 K – none observed post-annealing.
Br adatoms are mobile on the surface at >300 K --
form islands on the terraces and above steps.
(Br islands show no Cu surface state)

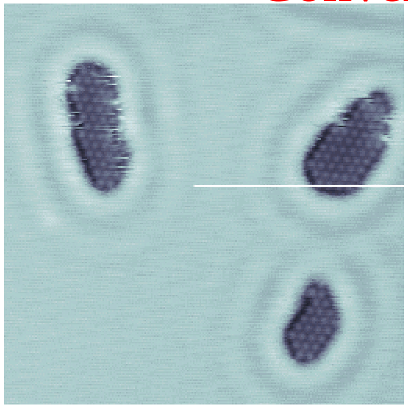
**Br islands are found only at half-multiples of Fermi wavelength**

PS Weiss

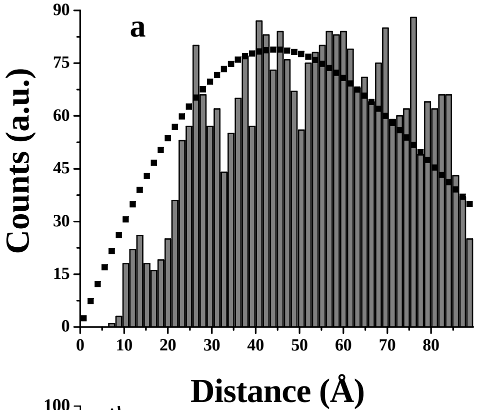
**Nanayakkara & Weiss**

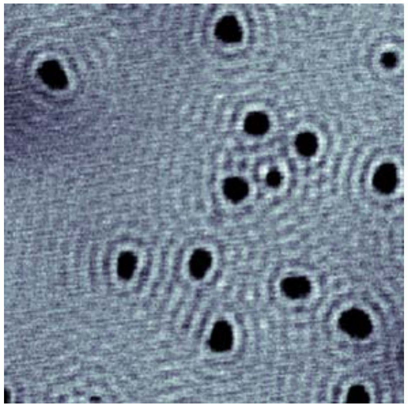
# Determine Inter-Island Potential

**Br islands are found only at half-multiples of Fermi wavelength: Convert distribution into inter-island potential**

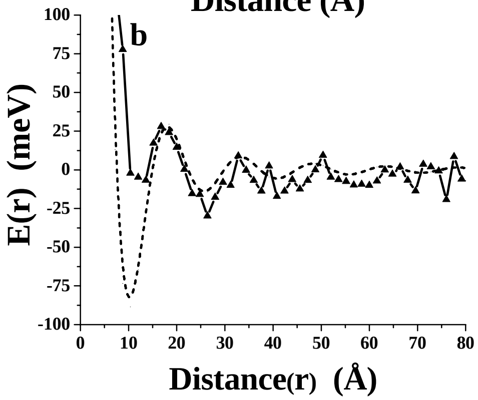


**Br on Cu{111}**
**176 Å × 176 Å**
**$V_{Sample}$ = ¯0.2 V**
**I = 50 pA**
**T = 4 K**



**Br on Cu{111}**
**420 Å × 420 Å**
**$V_{Sample}$ = ¯0.05 V**
**I = 10 pA**
**T = 4 K**




**Measure 3000 inter-island spacings**
**(preliminary analysis)**

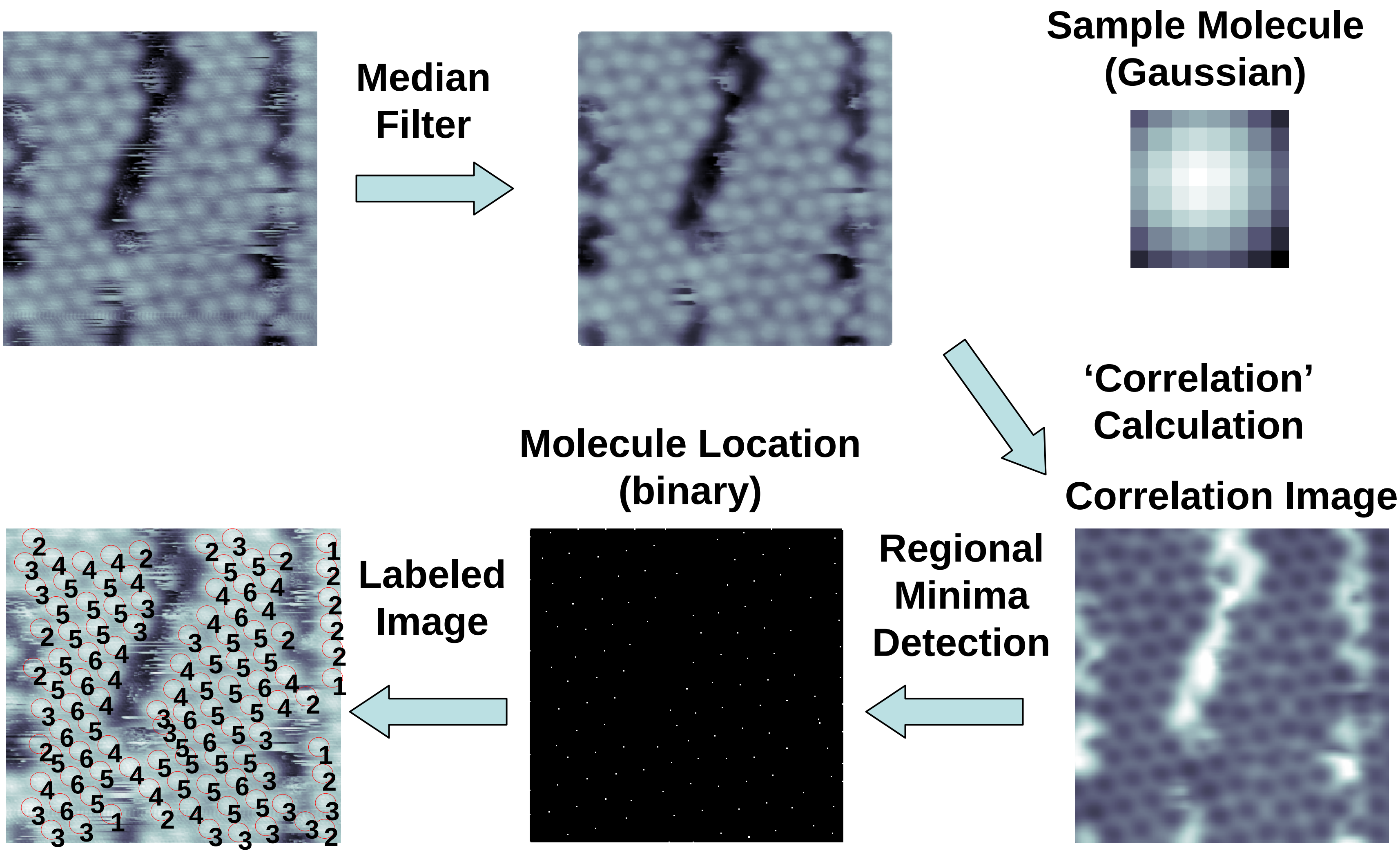
**Coherence length (~40 Å) reflects high temperature at which islands form.**

PS Weiss

**Nanayakkara & Weiss**

# Track Environment/Interaction-Dependent Motion: Benzene/Au{111} at 4 K

**Automated recording and analysis of tens of thousands of molecular positions to separate types of motion and to quantify interactions**



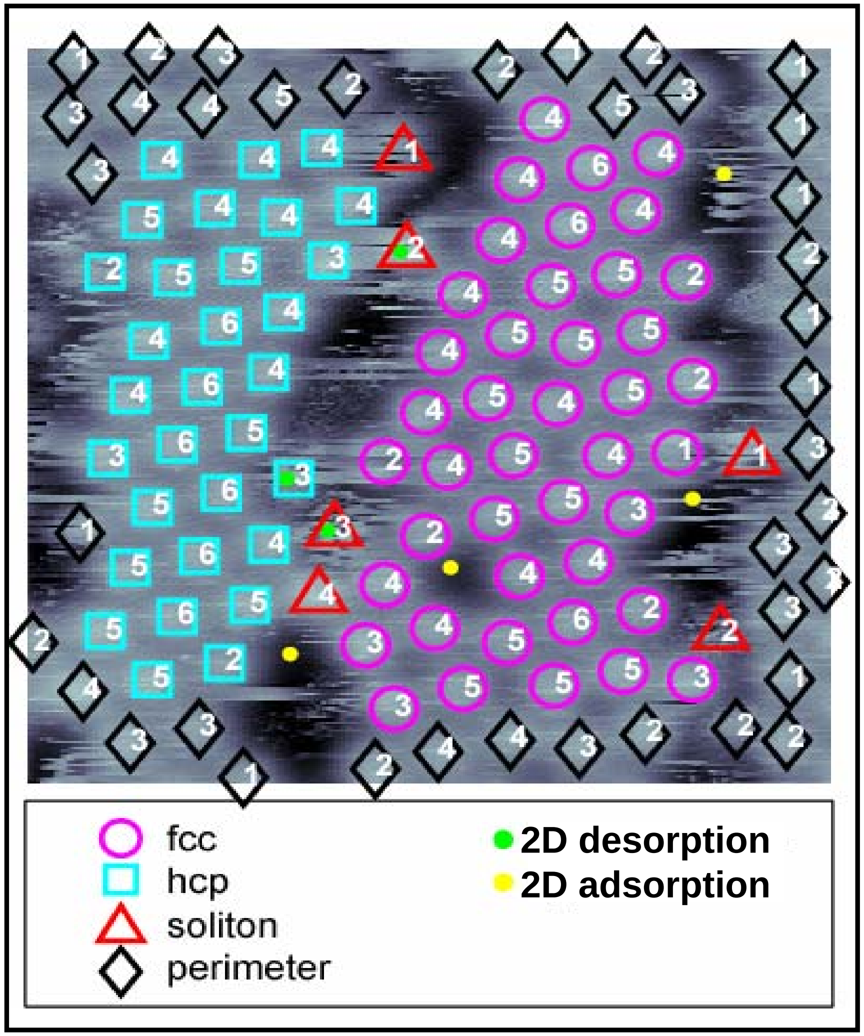

PS Weiss

**Sykes, Mantooth, Han, Donhauser & Weiss, *JACS* <u>127</u>, 7255 (2005)**

# Track and Analyze Motion: Benzene/Au{111} at 4 K

**Motion is very structure and environment dependent**

**79 Å x 79 Å**
**$V_{sample}$ = $^{+}$0.3 V**
**I = 5 pA**




**Coverage = 0.9 monolayers**

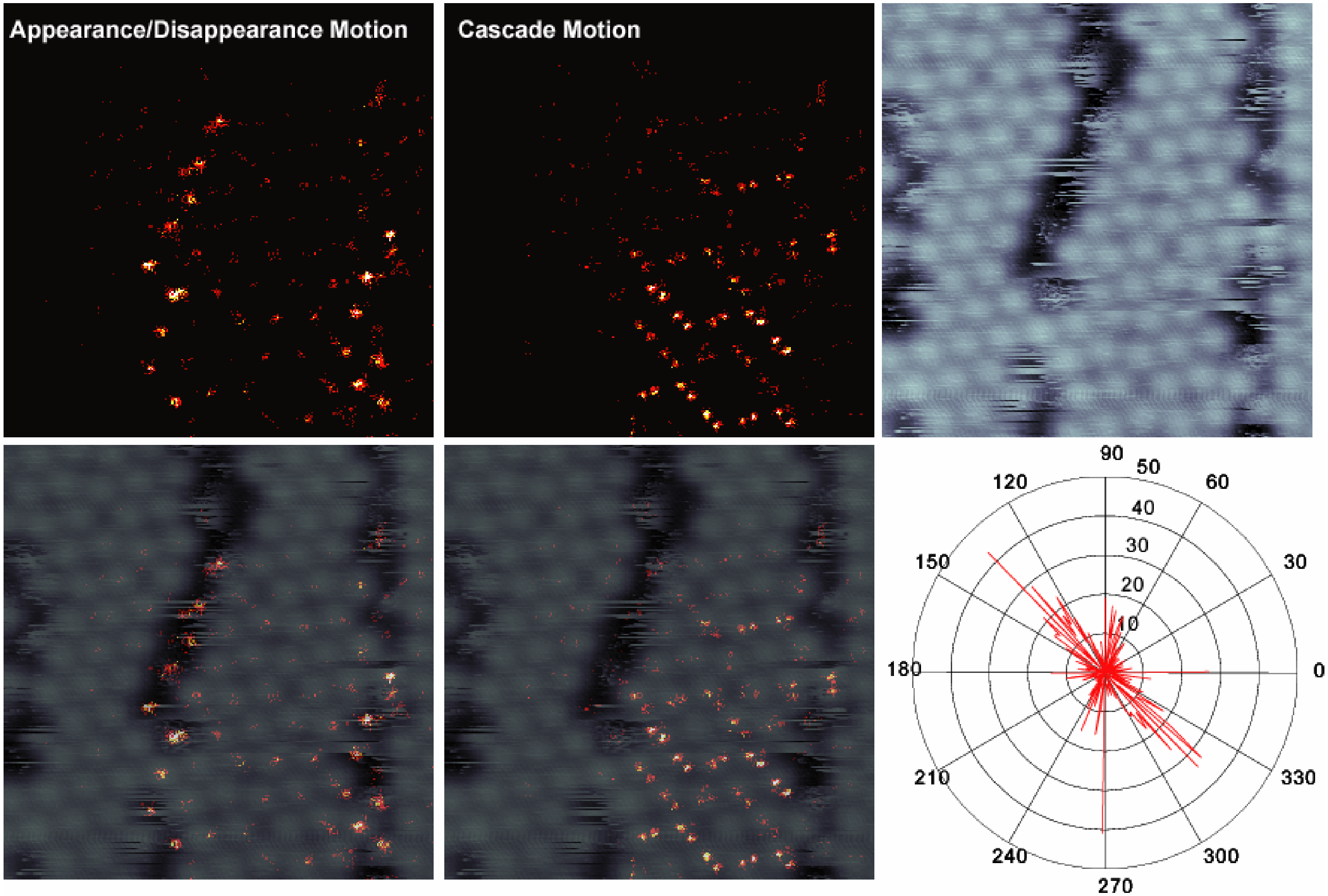
**Assign position of every molecule and determine frame to frame changes**

PS Weiss

**Sykes, Mantooth, Han, Donhauser & Weiss, *JACS* 127, 7255 (2005)**

# Observe and Understand Correlate Motions (Cascades)

**Distinguish and highlight most likely motions and direction of motion.**



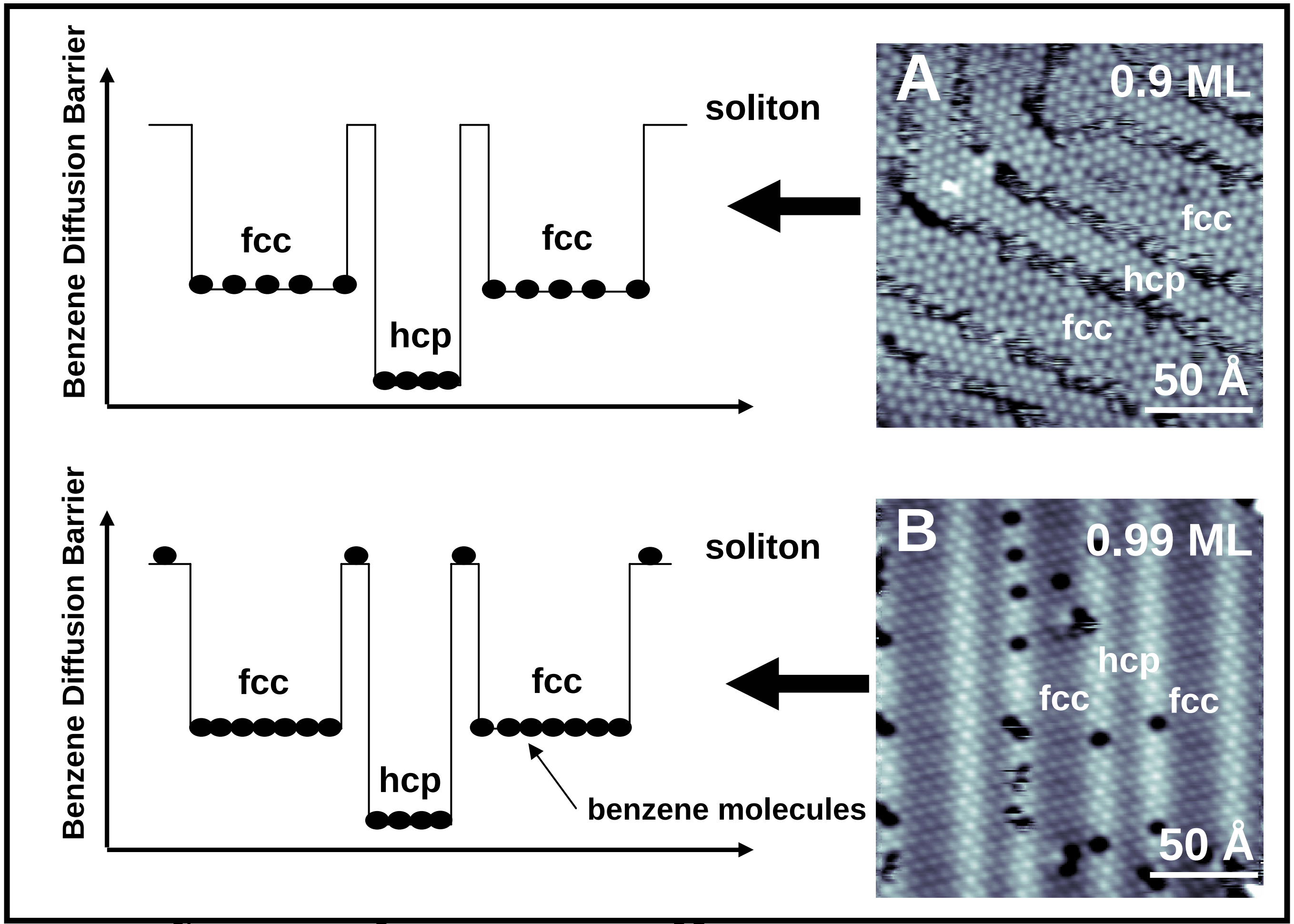

**77 Å x 77 Å, $V_{sample}$= $^{+}$1 V, I = 20 pA, T = 4 K, 0.9 monolayers**

PS Weiss

**Han, Mantooth, Sykes, Donhauser & Weiss, *JACS* 126, 10787 (2004)**

# Determine Adsorption and Interaction Strengths

**From probability of motion, determine binding strengths.**




| | fcc | hcp | soliton | |
|---|---|---|---|---|
| $\Delta E_{B\text{-}Au}$ = | 14.15(1) | 14.73(2) | <13.66(2) | kJ/mole |

$\Delta E_{Tip}$ = 0.384(3) kJ/mole, $\Delta E_{B\text{-}B}$ = 0.41(4) kJ/mole/molecule

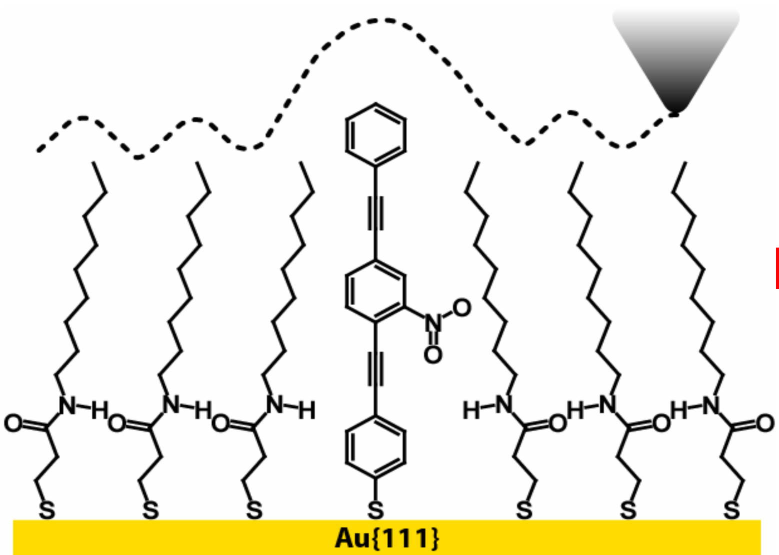
PS Weiss

Sykes, Mantooth, Han, Donhauser & Weiss, *JACS* 127, 7255 (2005)

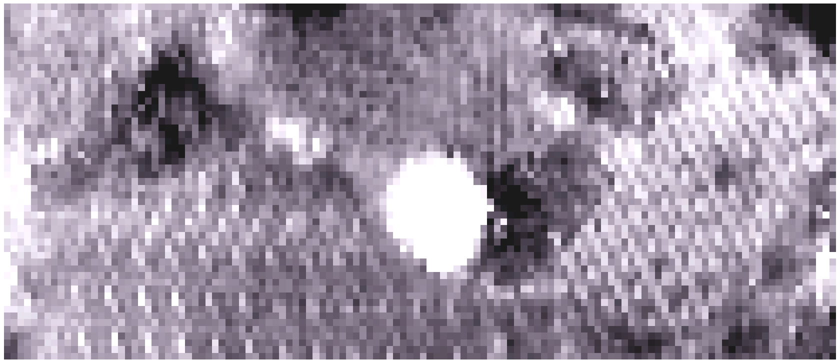
# Molecular Engineering of Molecular Switches

**Paul S. Weiss**
Departments of Chemistry & Physics
The Pennsylvania State University
http://www.nano.psu.edu/

**Insert molecular switches in defects in monolayers.**
**Test hypothetisized switching mechanisms**
**Hybridization change via molecular tilt**
**Can we control & stabilize switches? Y**

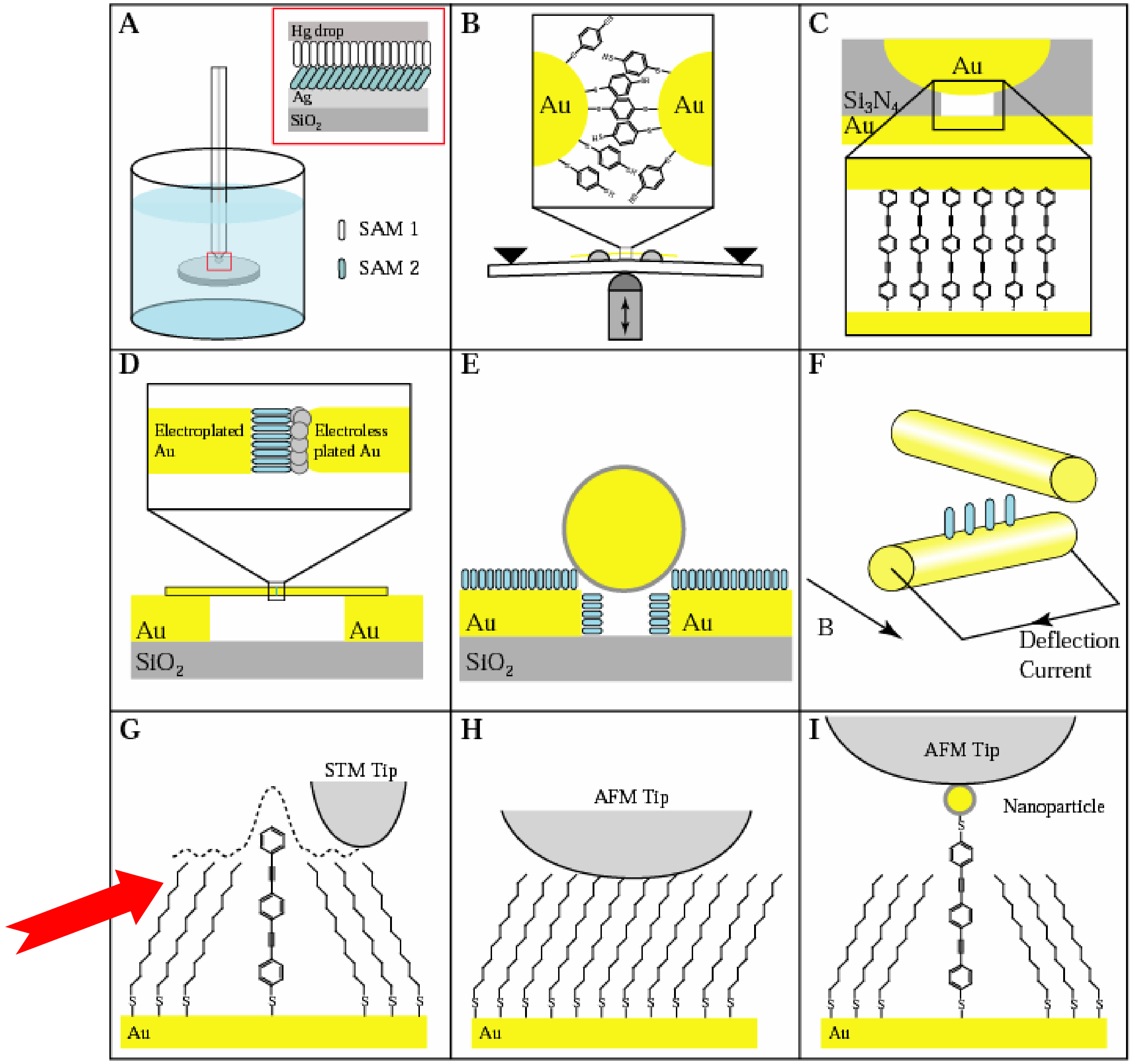



PS Weiss



**STM image of NPPB in 1ATC9 SAM**
**100 Å x 240 Å**
**$V_{sample}$ = +1.0 V, I = 2 pA**

# Measurements in Molecular Electronics




PS Weiss

**Mantooth & Weiss, *Proc. IEEE* <u>91</u>, 1785 (2003)**

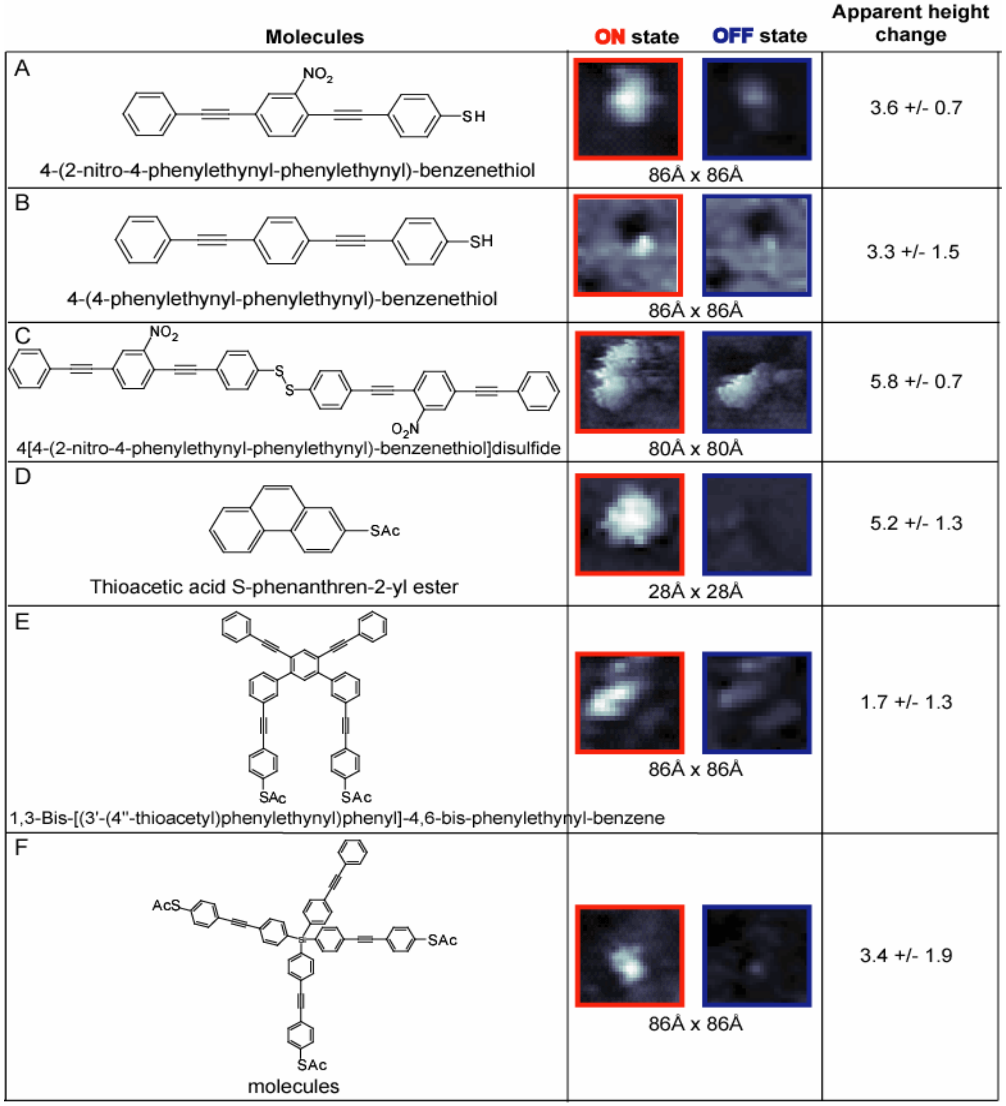
# What Functionality is Required for Molecular Switches?

**No nitro group**

**Insert only in pairs**

**No internal ring rotation**

**Single tilt axis**



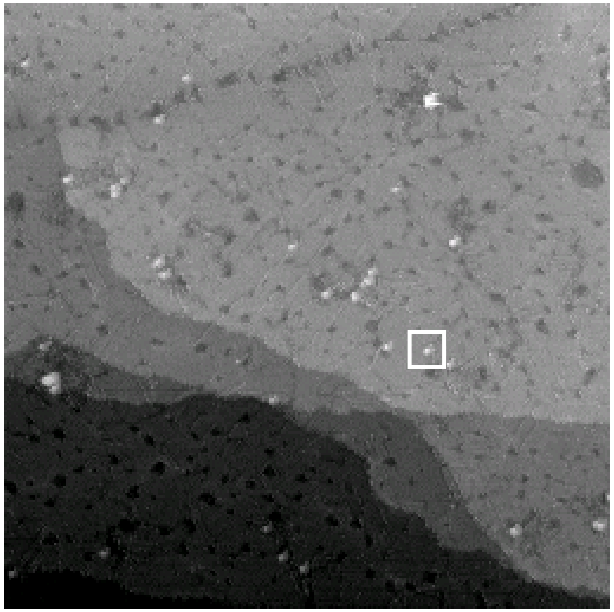

PS Weiss

**Moore, Dameron, Mantooth, Maya, Ciszek, Tour & Weiss, submitted**

# Record Many Isolated Switches Simultaneously

**Use control of matrix to insert isolated switches into field of view.**

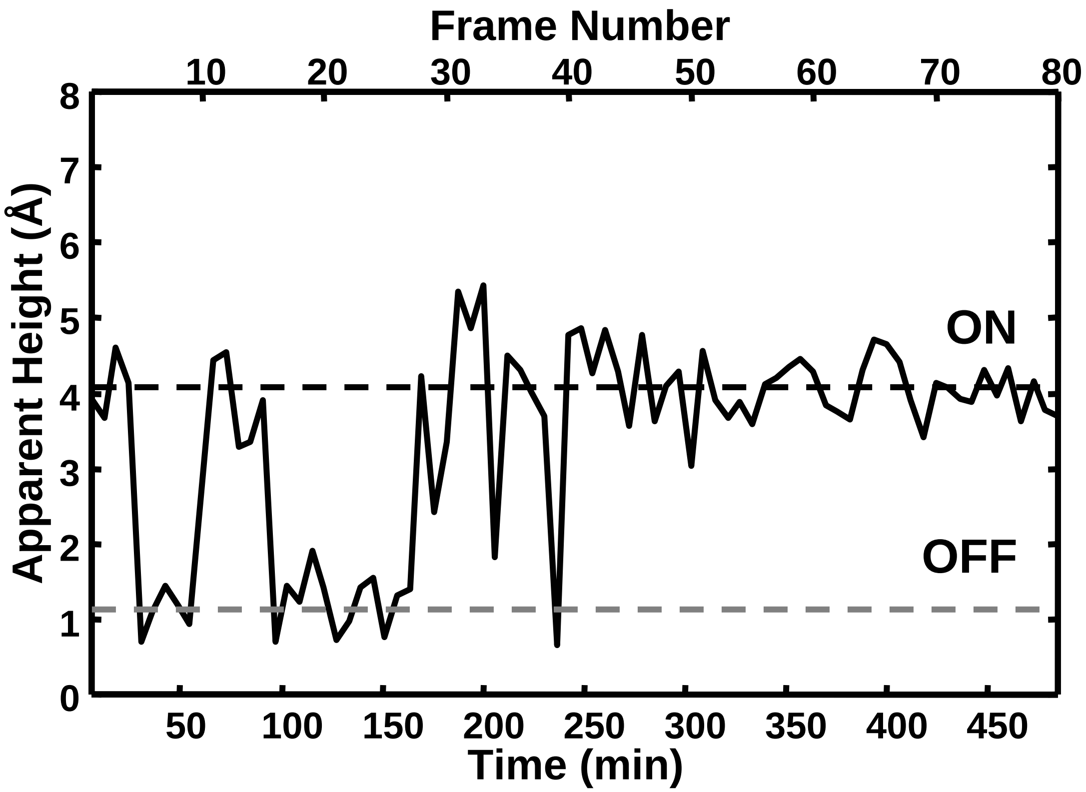
**Track automatically.**

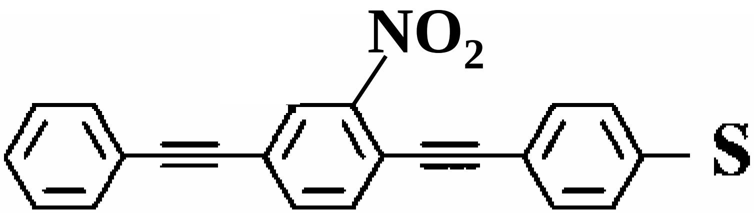


**1500 Å x 1500 Å**

**$V_{sample}$ = ¯1.4 V**

**I = 0.2 pA**

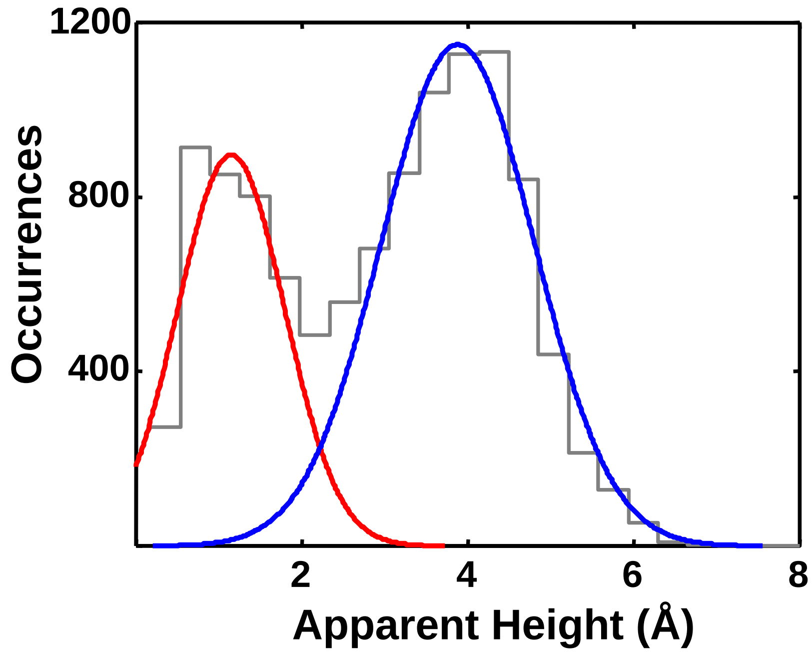


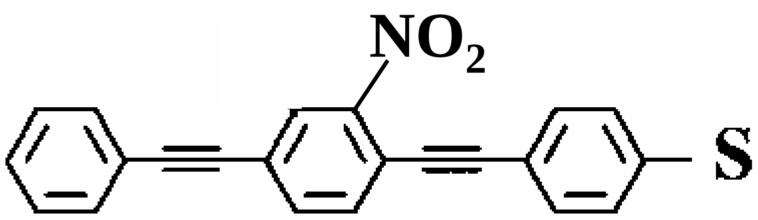




**Mantooth, Donhauser, Kelly &Weiss**
***Review of Scientific Instruments* 73, 313 (2002)**

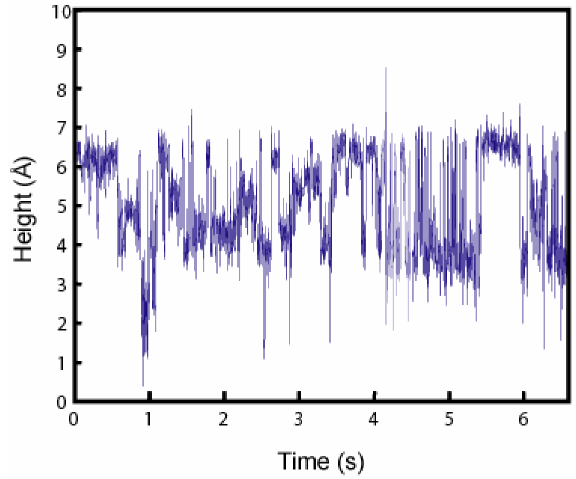
# Assemble Statistical Distributions at Different Time Scales

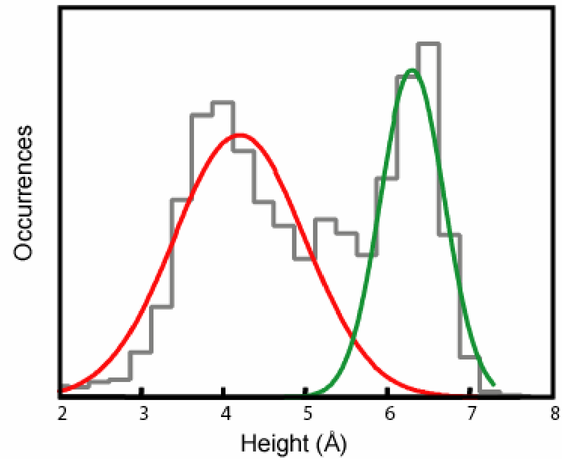
## Accumulated $10^0$-$10^5$ sec time scale measurements of ~50 isolated switches




## Real time measurements of an active switch



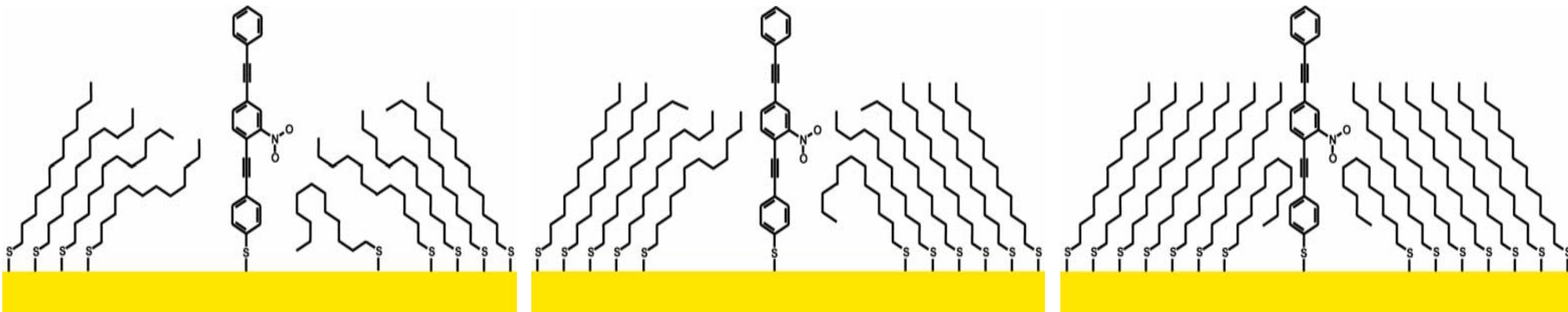

PS Weiss

**Donhauser & Weiss**

# Controlling Switching Activity

## Quality of host SAM matrix

Donhauser *et al.*, *Science* 292, 2303 (2001)

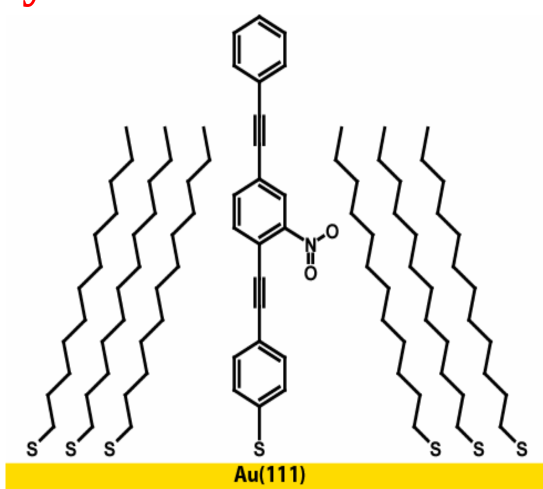


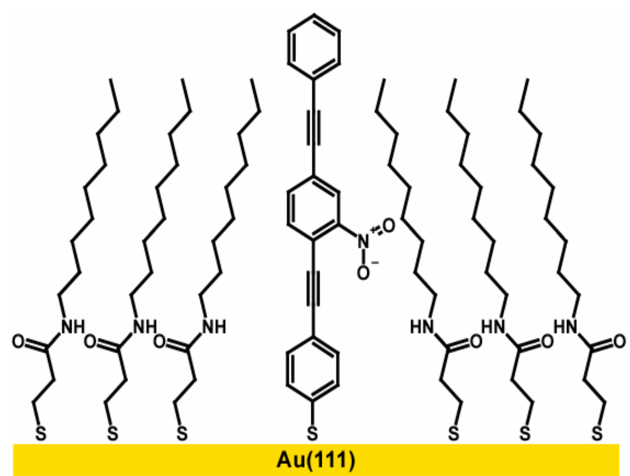
**Less ordered (5 min)** — **Standard (24 hr)** — **Vapor Annealed (24 hr)**

**High** ← **Switching Activity** → **Low**

## Chemistry of host SAM matrix

Lewis *et al.*, *JACS* submitted

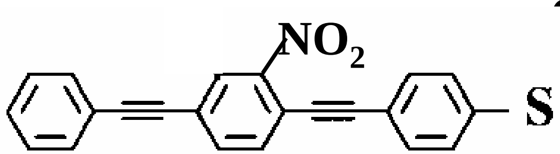


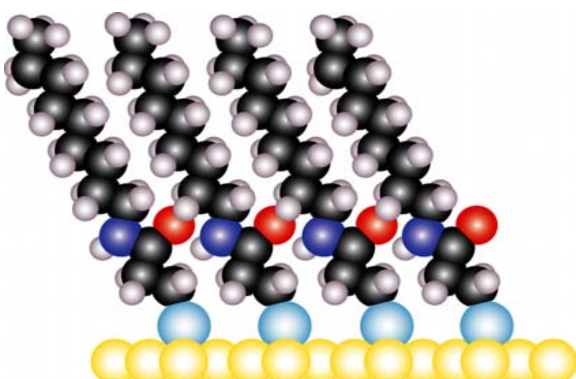



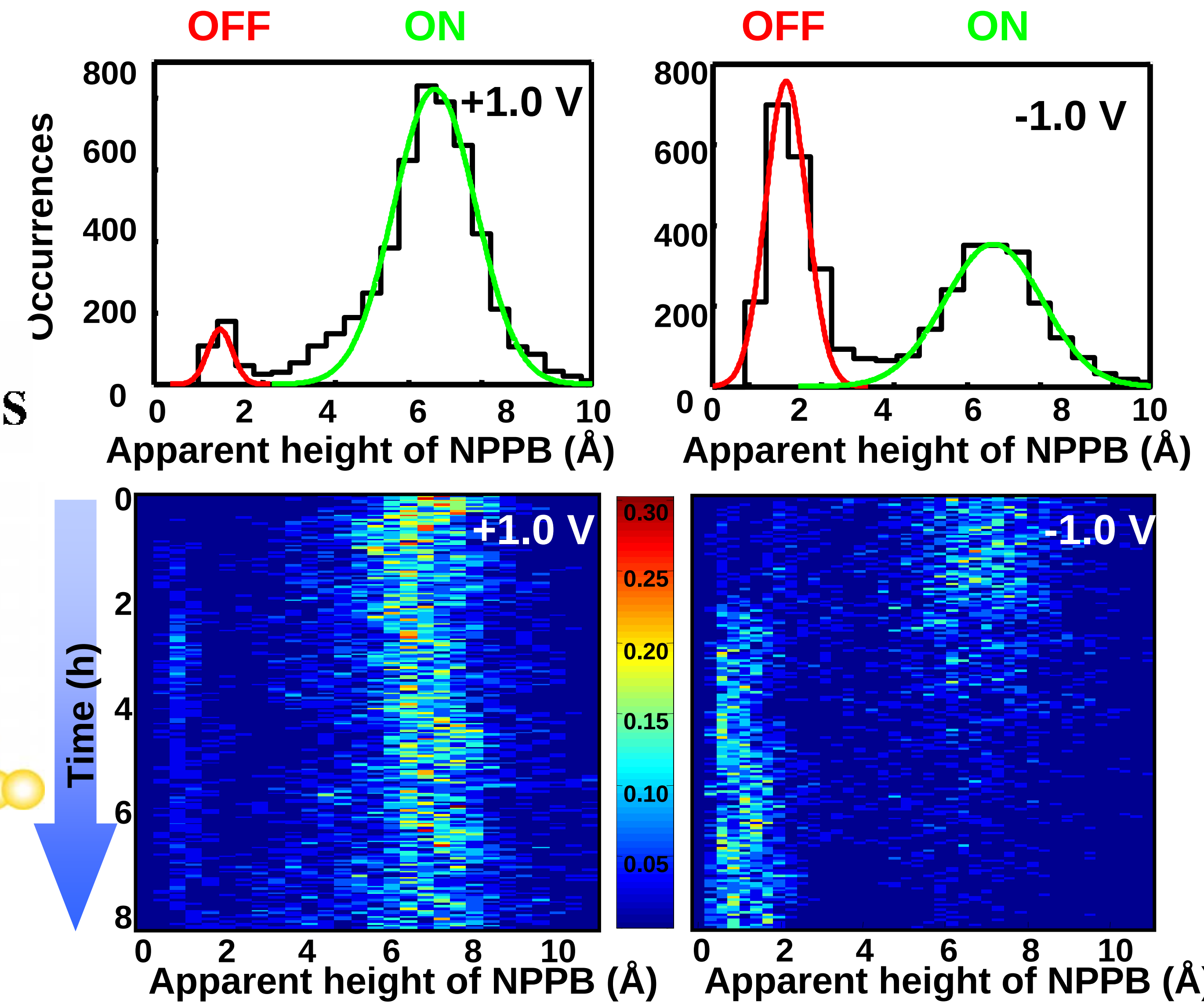
# Bias Dependent Switching

## Time histories of switches inserted in monoamide SAM

1500 Å x 1500 Å
$V_{sample}$ = ±1.0 V, 2.0 pA
200 frames (~9.5 h)
2 min 51 sec/frame



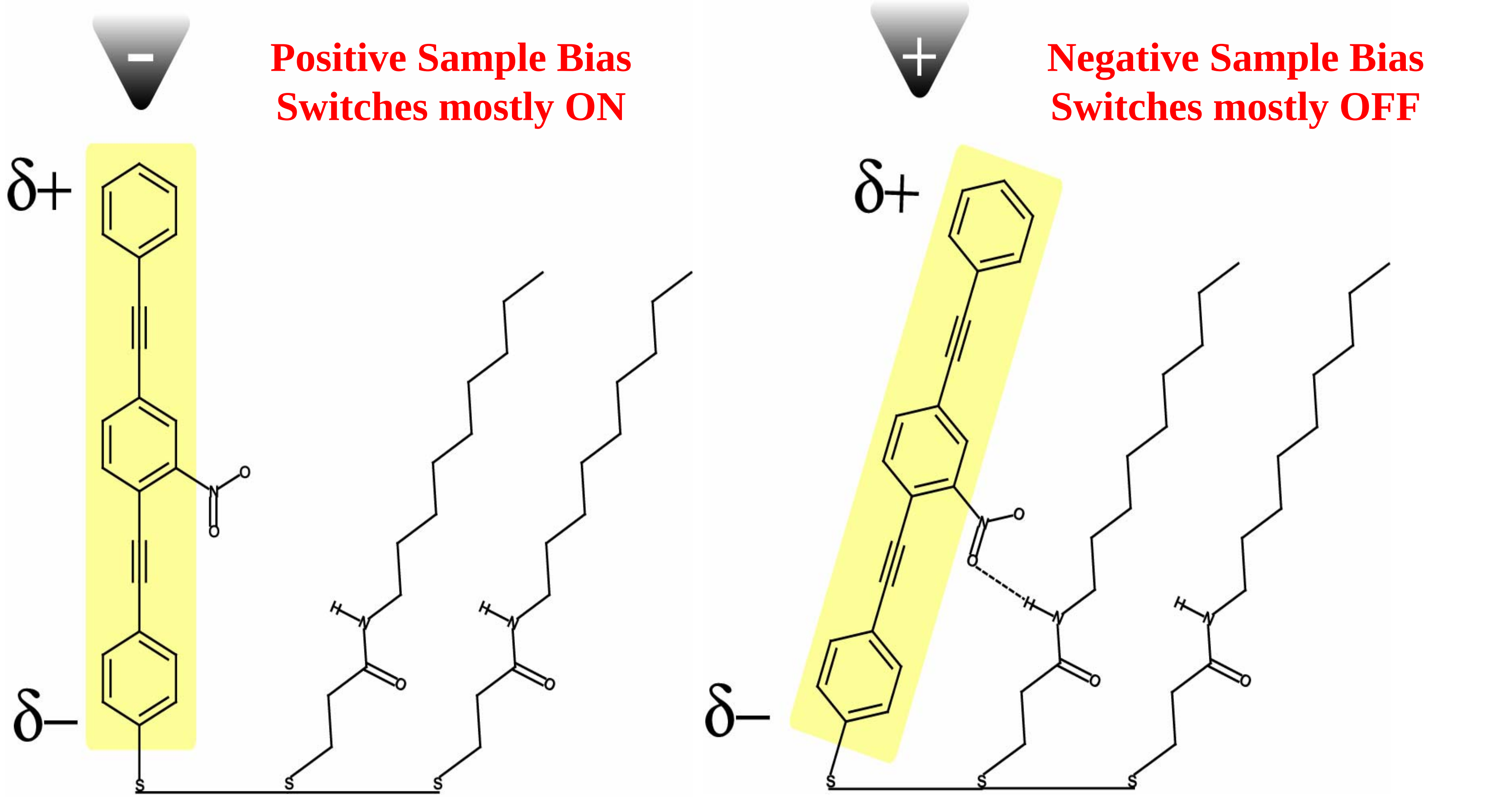






PS Weiss

Lewis, Inman, Yao, Tour, Hutchison & Weiss, *JACS* 126, 12214 (2004)

# Bias Dependent Switching Mechanism




**Switching is correlated to:**

**Handles for molecular design**

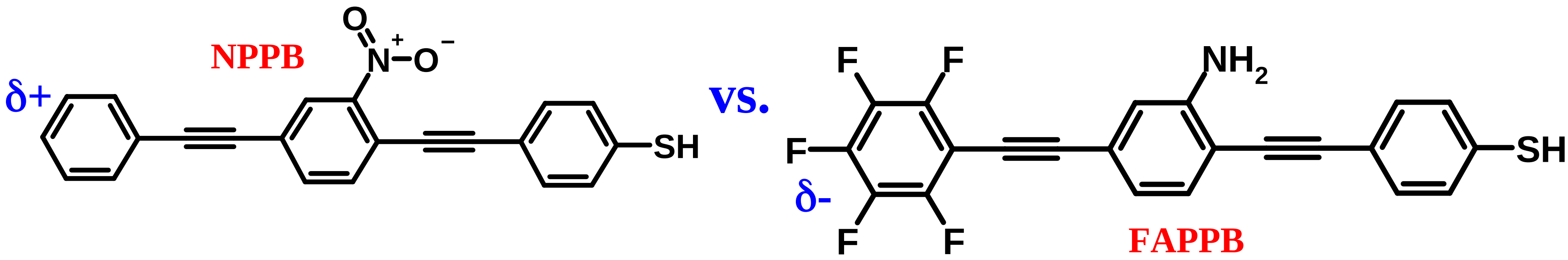
- **Interaction of electric field from STM tip and molecular dipole**
- **Hydrogen bonding**

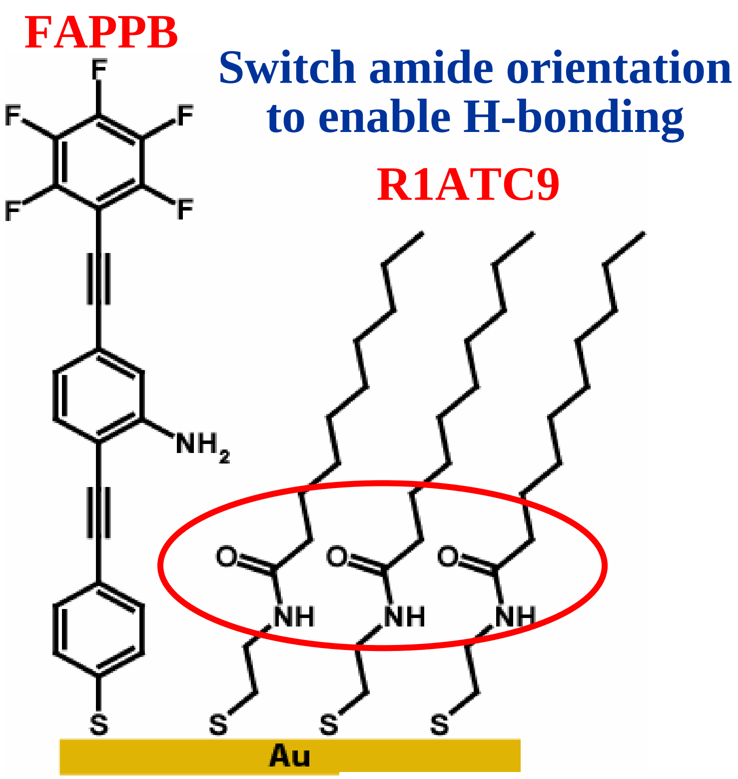
PS Weiss

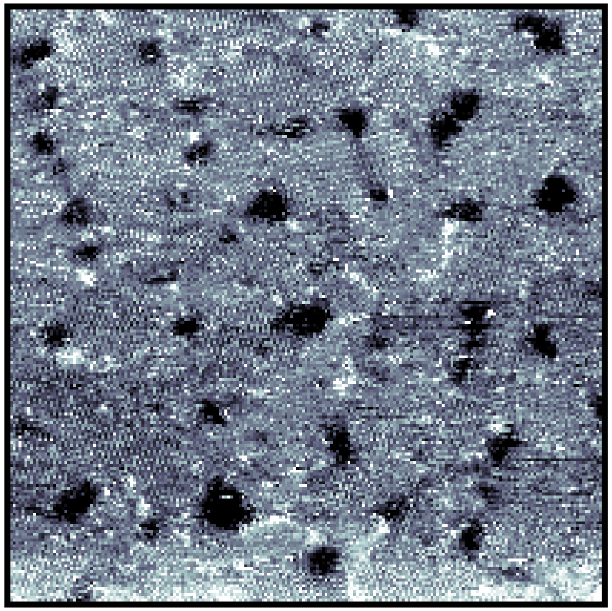
**Lewis, Inman, Yao, Tour, Hutchison & Weiss, *JACS* 126, 12214 (2004)**

# Control Switching with Electric Field Polarity

**Invert dipole to test hypothesis of switching via electric field**



485 Å x 485 Å

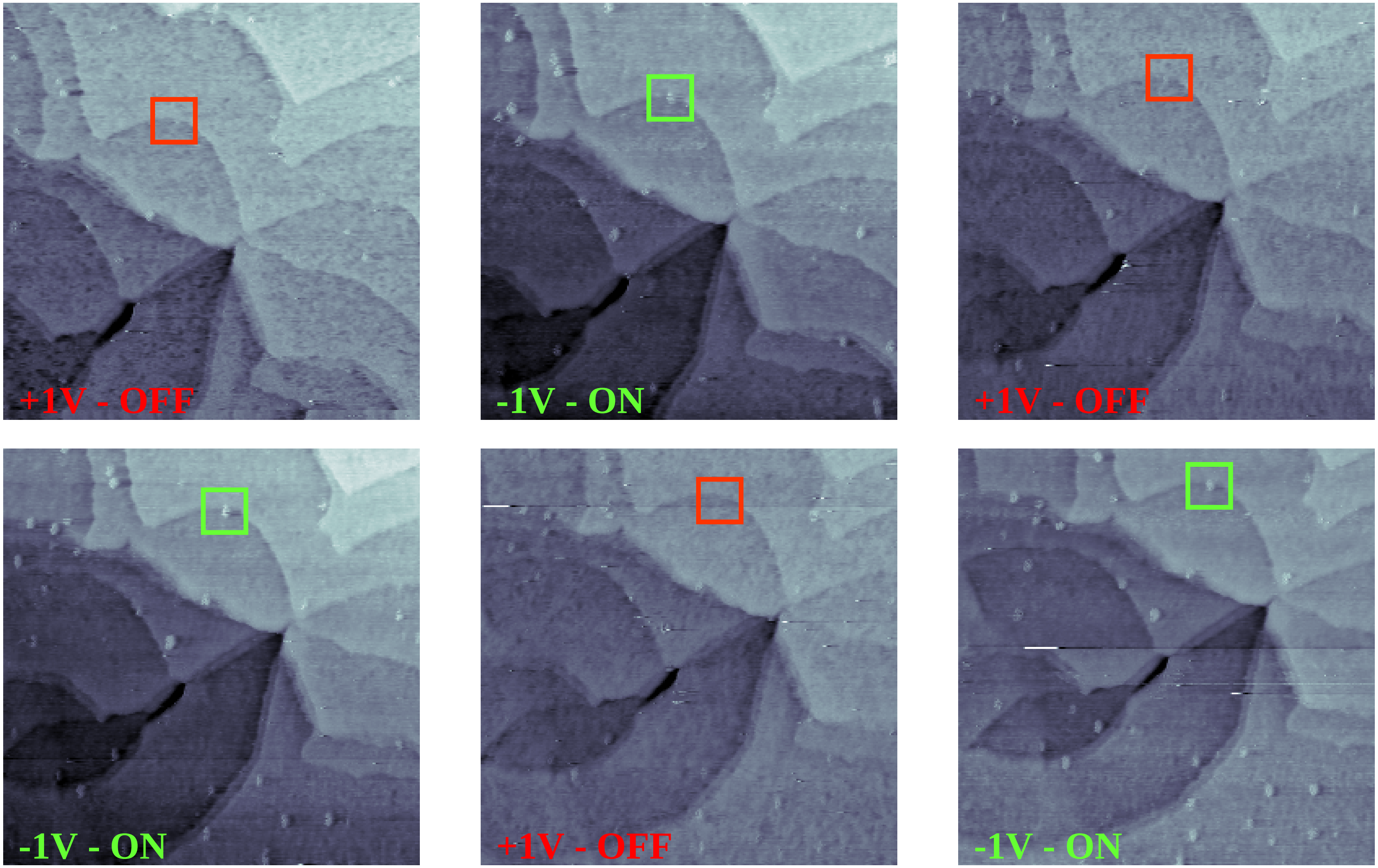
$V_{sample}$ = -1.0 V

I = 2.0 pA

PS Weiss

**Lewis, Tour, Hutchison & Weiss, in preparation**

# Control Switching with Electric Field Polarity




**FAPPB (inverted dipole) in R1ATC9 (matching H-bonding amide alkanethiolate)**
**4000 Å x 4000 Å, I = 2.0 pA**

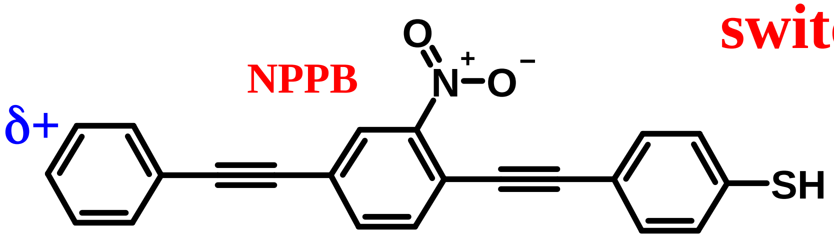
PS Weiss

**Lewis, Tour, Hutchison & Weiss**

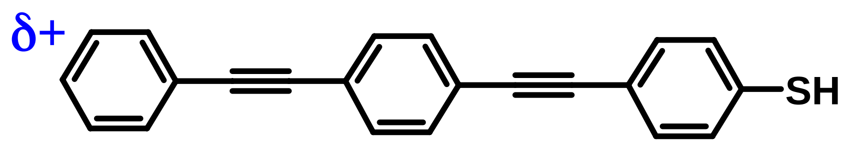
# Control Switching with Electric Field Polarity and Intermolecular Interactions

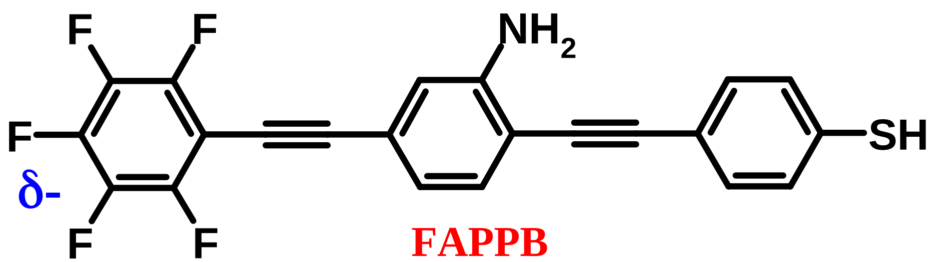
**Inverting switch dipole requires opposite electric field polarities for switching**

NPPB




PPB




FAPPB

| | NPPB | PPB | FAPPB |
|---|---|---|---|
| Hydrogen bonding | YES | NO | YES |
| Dipole moment | +4.3 D | +1.7 D | -3.7 D |
| Bias dependence | Positive – ON<br>Negative – OFF | NONE | Positive – OFF<br>Negative – ON |

PS Weiss

**Lewis, Tour, Hutchison & Weiss**